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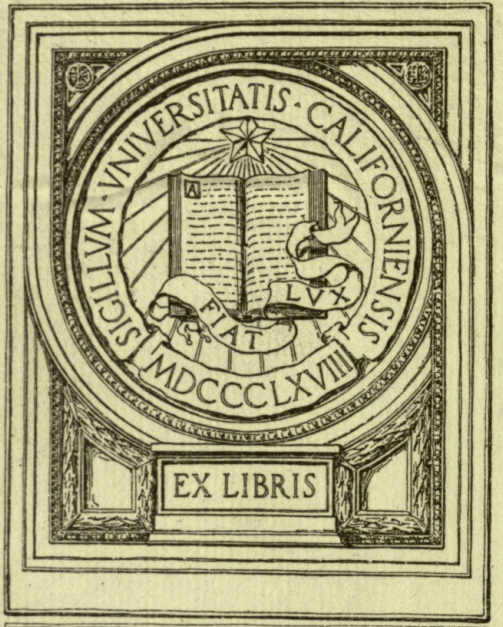

# A TREATISE ON CHEMISTRY.

A

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BY

H. E. ROSCOE F.R.S. AND C. SCHORLEMMER F.R.S.

PROFESSORS OF CHEMISTRY IN THE VICTORIA UNIVERSITY OWENS COLLEGE, MANCHESTER.

*VOLUME III.*

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES,

OR

## ORGANIC CHEMISTRY,

PART II.

"*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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# ORGANIC CHEMISTRY.

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# ORGANIC CHEMISTRY,

## OR THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

## PART II.

## COMPOUNDS CONTAINING DIVALENT RADICALS.

### DYAD ALCOHOL RADICALS.

THESE compounds differ from the monatomic alcohol radicals inasmuch as many exist in the free state. They form a homologous series, the first term being ethylene, $C_2H_4$, formerly called olefiant gas. For this reason, at Guthrie's suggestion, the hydrocarbons having the general formula $C_nH_{2n}$ are termed the *olefines*.[1]

451 *General properties of the Olefines.* The lower members of this series are, like the lower paraffins, gases at the ordinary temperature. The next members are volatile liquids, whose boiling-points rise regularly with every increment of $CH_2$ until the higher members are reached; these are solid bodies, crystallizing at the ordinary temperature. The olefines are at once distinguished from the paraffins by their reaction with chlorine and bromine, as they combine directly with these elements, even in the dark, with evolution of heat, to form dichlorides or dibromides, and these latter bodies are readily transformed, by double decomposition,

[1] *Journ. Chem. Soc.* [1], xii. 109.

into other compounds of the dyad alcohol radicals. For effecting these conversions methods are used similar to those employed for the preparation of the compounds of the monad alcohol radicals from their haloid ethers.

Attempts to prepare other compounds of dyad radicals from the haloid ethers were first made in 1840 by Löwig and Weidmann. They acted upon ethylene chloride with potassium sulphide and potassium hydrosulphide, obtaining ethylene sulphide and ethylene hydrosulphide,[1] the true relationships of which were however at that time not fully recognised.[2]

In 1855 Buff,[3] and at the same time Sonnenschein and Meyer,[4] prepared ethylene thiocyanate, whilst a year afterwards Wurtz made the memorable discovery of the existence of ethylene alcohol (see part i. p. 27). He and several of his pupils then showed that this body is the first term of a series of homologues, and soon made us acquainted with a large number of very interesting derivatives.

The olefines also combine directly with the hydracids of the chlorine group. Ethylene and hydriodic acid form ethyl iodide, whilst the olefines containing more than two atoms of carbon yield secondary or tertiary haloid ethers, as has already been stated (part i. p. 182). Some olefines also combine directly with water, with formation of the tertiary alcohols (part i. p. 186). Moreover they combine with hypochlorous acid, bodies termed *chlorhydrates* or *chlorhydrins* being thus formed, such as *ethylene chlorhydrin*, $C_2H_4Cl.OH$, and these may be considered to be monochlorinated alcohols of the monad radicals. The olefines likewise combine with nitrogen tetroxide.

452 *Constitution of the Olefines.* Owing to the readiness with which the olefines undergo direct combination, they have been termed non-saturated hydrocarbons, an expression which points to the assumption that they contain free combining units. This view was formerly accepted by some chemists, whilst others adopted the idea that the olefines are saturated compounds, but that they contain one atom of carbon which acts not as a tetrad but as a dyad. According to a third hypothesis, now generally adopted, two of the carbon atoms in the olefines are linked together by two combining units, and this double linkage is changed into a single linkage by the action of the elements of the chlorine group or their hydracids. According to

[1] *Pogg. Ann.* xlix. 123.
[2] Kekulé, *Lehrb.* i. 643.
[3] *Ann. Chem. Pharm.* c. 229.
[4] *Journ. Prakt. Chem.* lxv. 259.

the first of these hypotheses, the simplest olefine, ethylene, $C_2H_4$, ought to exist in two forms:

$$\begin{array}{ll} CH_3 & -CH_2 \\ | & | \\ =CH. & -CH_2. \end{array}$$

We are however acquainted with only one ethylene, and all experiments made for the purpose of obtaining an isomeric hydrocarbon have proved abortive.[1] That the well known body ethylene is not represented by the first of the above two formulæ, and therefore also that it is not represented by the formula $CH_3—CH$, which assumes the existence of a dyad carbon atom, is proved by the fact that the above named ethylene chlorhydrin yields on oxidation chloracetic acid:

| Ethylene Chlorhydrate. | Chloracetic Acid. |
|---|---|
| $CH_2Cl$ | $CH_2Cl$ |
| $CH_2.OH.$ | $CO.OH.$ |

Hence ethylene possesses the constitution assigned to it by the second formula, or it contains the two carbon atoms doubly linked.

A further argument against the existence of either free combining units or dyad carbon is found in the fact that only one propylene, $C_3H_6$, is known, whilst according to the first of these hypotheses the four following are possible:

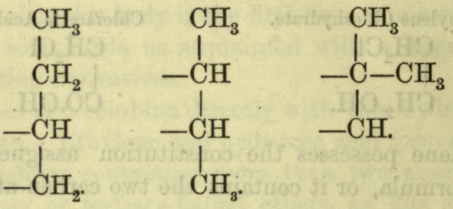
$$\begin{array}{llll} CH_3 & -CH_2 & CH_3 & CH_3 \\ | & | & | & | \\ -CH & CH_2 & =C & CH_2 \\ | & | & | & | \\ -CH_2. & -CH_2. & CH_3. & =CH. \end{array}$$

If, on the other hand, we assume that the hydrocarbon contains a dyad carbon atom, the atoms can only arrange themselves according to the third or fourth formula. That, however, this is not the case follows from the fact that propylene is obtained by the withdrawal of the elements of hydriodic acid from both primary and secondary propyl iodide, and that consequently on the assumption of free combining units, only the first of these formulæ can explain its constitution.

Again, whilst we are acquainted with only one ethylene and

[1] Tollens, *Ann. Chem. Pharm.* cxxxvii. 311; L. Meyer, *ib.* cxxxix. 285; Frankland and Dobbin, *Journ. Chem. Soc.* 1878, i. 545.

one propylene, three butylenes, $C_4H_8$, exist, and the assumption that the olefines each contain two carbon atoms doubly linked stands in complete accordance with this fact, whilst on the other hypotheses a larger number of butylenes are possible. These three butylenes are obtained by removing the elements of hydriodic acid from the well known butyl iodides. The normal primary iodide yields a butylene different from that obtained from the secondary iodide. Both olefines however unite with hydriodic acid to form the secondary iodide. A third butylene is formed both from isobutyl iodide and from the tertiary iodide, and it combines with hydriodic acid to form the latter body. If we now assume that these olefines contain free combining units, their constitution can only be represented by the following formulæ:



In other words it is proved in this as in all other cases that the carbon atoms which are not saturated with hydrogen are the two neighbouring ones and the simplest, and, therefore, the most probable hypothesis is that these two atoms are connected together by double linkage.

When the olefines are oxidized by potassium bichromate and dilute sulphuric acid, they decompose in a similar way to the secondary or tertiary alcohols, and the division of the molecule, except in the case of ethylene, always takes place where the double linkage occurs. Potassium permanganate in aqueous or acid solution acts in a similar way, but at the same time bibasic acids are mainly produced.

As examples the following may be quoted:

Propylene. $CH_3.CH{=}CH_2$.

Isobutylene. $(CH_3)_2C{=}CH_2$.

Propyl-ethylene. $CH_3.CH_2.CH_2.CH{=}CH_2$.

Methyl-propyl-ethylene. $CH_3.CH_2.CH_2.CH{=}CH.CH_3$.

Ethyl-dimethyl-ethylene. $CH_3.CH_2.CH{=}C(CH_3)_2$.

Tetramethyl-ethylene. $(CH_3)_2C{=}C(CH_3)_2$.

Of these, the two first yield on oxidation carbon dioxide, acetic acid, and formic acid, isobutylene yielding acetone in addition. Propyl-ethylene yields normal butyric acid and formic acid, and the first of these acids is formed together with acetic acid from methyl-propyl-ethylene, whilst ethyl-dimethyl-ethylene yields propionic acid, and acetone or acetic acid. On the other hand, tetramethyl-ethylene yields only the two latter compounds.

The above examples serve to illustrate the nomenclature of the olefines, their names being obtained by the addition of the syllable *-ene* to the name of the corresponding monad radical. Another nomenclature which is sometimes adopted is to change the vowel *a* in the terminal syllable of the paraffin into *e*, eth*ane* thus becoming eth*ene*, &c. As all the olefines may be looked upon as derivatives of ethylene, propylene may be termed methyl-ethylene, and isobutylene, dimethyl-ethylene. This form of nomenclature is especially useful for the distinction of isomeric olefines, as the above examples indicate.

453 *Formation of the Olefines.* Olefines are formed in several ways. They are obtained from the alcohols of the monad radicals by the action of dehydrating agents, such as sulphuric acid, phosphorus pentoxide, zinc chloride, &c.

The haloid ethers of the alcohol radicals are converted into the olefines when they are heated with alcoholic potash:

$$C_4H_9I + KOH = C_4H_8 + KI + H_2O.$$

The secondary and tertiary compounds readily undergo decomposition in this way, some of the latter class even decomposing spontaneously at temperatures considerably above their boiling-points. The primary haloid ethers which are attacked by potash with greater difficulty, always yield, together with the olefines, a mixed ether, whilst, secondary chlorides yield with potassium acetate and glacial acetic acid under pressure, not only the acetic ethers but also an olefine (Schorlemmer). The haloid ethers are likewise converted into olefines by heating with oxide of lead to 220°.[1]

The olefines, moreover, may be prepared synthetically. For example, the butylene termed ethyl-ethylene may be obtained by the action of zinc-ethyl on monobrom-ethylene:

$$2C_2H_3Br + Zn(C_2H_5)_2 = 2C_2H_3.C_2H_5 + ZnBr_2.$$

Allyl iodide, $C_3H_5I$, similarly treated yields a pentylene, $CH_2{=}CH.CH_2.CH_2CH_3$, which is propyl-ethylene.

[1] Eltekow, *Journ. Russ. Chem. Ges.* p. 89.

The production of the olefines in various preparations of the paraffins, as well as by heating the solid paraffins under pressure, has already been mentioned (see part i. p. 137).

The hydrocarbons which are evolved when cast-iron is dissolved in dilute acids also contain olefines;[1] and lastly, these bodies are found amongst the products of the destructive distillation of many organic compounds, and hence occur in coal-gas, coal-tar, wood-tar, &c.

Zinc chloride or sulphuric acid easily converts the olefines into polymeric modifications, and hence when they are prepared from the alcohols by means of these bodies, polymeric hydrocarbons are generally formed. In this formation a double decomposition between the olefine and unattacked alcohol takes place.[2] Thus, for example, by the action of sulphuric acid on trimethyl-carbinol, di-isobutylene and tri-isobutylene are formed:

$$C_4H_8 + C_4H_{10}O = C_8H_{16} + H_2O.$$

$$C_8H_{16} + C_4H_{10}O = C_{12}H_{24} + H_2O.$$

The same products are obtained by heating isobutylene, tertiary-butyl iodide, and lime to 100°.[3] The constitution of these and other polymeric olefines will be discussed under their several heads.

454 *Substitution-products of the olefines.* Inasmuch as the elements of the chlorine group unite directly with the olefines, these bodies naturally do not directly give rise to substitution-products, although such compounds may be obtained indirectly. For example, the four atoms of hydrogen in ethylene may be replaced successively by chlorine, by combining the olefine with chlorine, and then heating the ethylene dichloride with alcoholic potash:

$$C_2H_4Cl_2 + KOH = C_2H_3Cl + KCl + H_2O.$$

The monochlor-ethylene thus formed again combines with chlorine to form monochlor-ethylene dichloride, and this is converted by alcoholic potash in dichlor-ethylene, and so on.

455 *Glycols.* This name is given to the class of diatomic alcohols, the first term of which series is ethylene alcohol or glycol, $C_2H_4(OH)_2$. This was first obtained in 1856 by Wurtz, a discovery

[1] Hahn, *Ann. Chem. Pharm.* cxxix. 57; Williams, *Silliman's Amer. Journ.* [3], vi. 363; Cloëz, *Compt. Rend.* lxxviii 1565.
[2] Butlerow, *Ann. Chem. Pharm.* clxxxix. 47.
[3] Lermontow, *Ib.* cxcvi. 116.

which was soon followed by that of several of its homologues. Up to that time, only the alcohols of monad radicals were known, with the single exception of glycerin, $C_3H_5(OH)_3$, which, as Berthelot had pointed out, is an alcohol of a triad radical. It appeared therefore to Wurtz not unlikely that an alcohol might exist intermediate between alcohol and glycerin. This was borne out by experiment, and the body thus obtained he termed *glycol*, "pour marquer la double analogie qui les relie à la glycérine d'une part, à l'alcool de l'autre." [1]

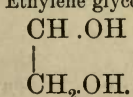
The glycols may be obtained from the haloid ethers of the dyad radicals, in a similar way to that by which the common alcohols are obtained from their corresponding ethers. Several other modes of preparation will be described hereafter.

After Wurtz had prepared the four first glycols, he made the singular observation that the boiling-points of these bodies, in opposition to those of members of the other homologous series, do not rise but, on the contrary, diminish for every increment of $CH_2$, as follows:

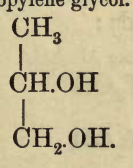
| | | B.P. |
|---|---|---|
| Ethylene glycol, | $C_2H_6O_2$ | 197°·5 |
| Propylene glycol, | $C_3H_8O_2$ | 188° |
| Butylene glycol, | $C_4H_{10}O_2$ | 183° |
| Amylene glycol, | $C_5H_{12}O_2$ | 177° |

This apparently anomalous fact has since been very satisfactorily explained, for the constitution of the above-named bodies are, in fact, not analogous. That this is the case is seen from the following:

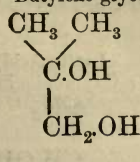
Ethylene glycol.



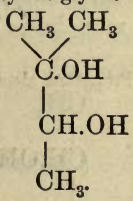
Propylene glycol.



Butylene glycol



Amylene glycol.

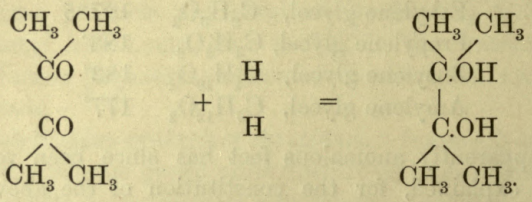


[1] *Ann. Chim. Phys.* [3], lv. 402.

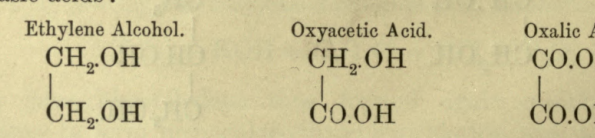
Ethylene glycol, according to this, is a primary alcohol; propylene glycol, on the other hand, is a primary-secondary compound; whilst the third alcohol, also termed isobutylene alcohol, is a primary-tertiary alcohol; and amylene glycol is a secondary-tertiary alcohol.

The primary alcohol, trimethylene-glycol, $CH_2(OH).CH_2CH_2(OH)$, isomeric with propylene-glycol boils at 216°, from which it appears that, in the case of the normal primary glycols, the boiling-point rises in exactly the same ratio as it does in the case of the corresponding alcohols of the normal series.

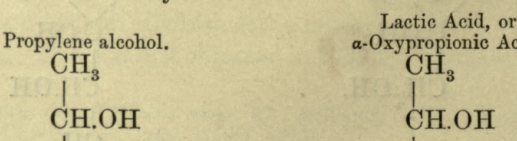
456 *Pinacones.* In addition to the foregoing, we are also acquainted with glycols which are only secondary, or only tertiary, alcohols. The tertiary glycols, which are termed *pinacones*, are easily obtained synthetically from the ketones by bringing them in contact with nascent hydrogen, when, of course, a part of the ketone passes over into the secondary alcohol, a result which may be to a great extent prevented by keeping the ketone out of solution. Common acetone yields the simplest pinacone or tetramethyl-ethylene alcohol:



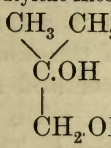
The glycols yield on oxidation, according to their constitution, different products. Those which are only primary alcohols, are converted first into monobasic, and afterwards into dibasic-acids:



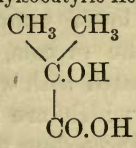

Primary-secondary, and primary-tertiary glycols yield, as first-product, a monobasic oxyacid:



Isobutylene Alcohol.



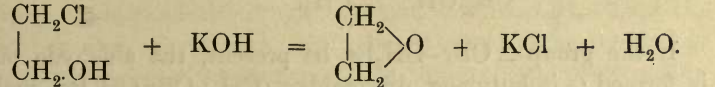
Oxyisobutyric Acid.



The oxyacids thus obtained are considered in the following chapter.

The secondary glycols yield on oxidation two molecules of a fatty acid, whilst the tertiary alcohols or pinacones are first reconverted into the ketones from which they originated.

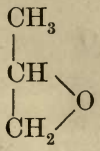
457 *Oxides.* The first product obtained by the action of hydrochloric acid on a glycol is a chlorhydrin, one of the hydroxyls being replaced by chlorine. These compounds which are half chlorides and half alcohols, and which, as has been stated, may also be obtained by the direct union of the olefines with hypochlorous acid, are easily attacked by caustic potash, and thus the oxide is formed :



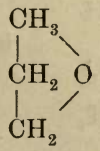
The oxide in the above case is isomeric with acetaldehyde which, as we have seen, may be regarded as the oxide of a dyad radical *ethidene*, $=CH.CH_3$.

The ketones, like the aldehydes, behave in many respects like oxides of dyad radicals, and hence in the propylene series we have the following four oxides:

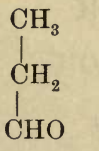
Propylene Oxide.



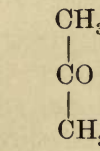
Trimethylene Oxide.



Propionaldehyde, or Propidene Oxide.



Acetone, or Dimethylmethylene Oxide.



It is a remarkable fact that the glycols are not converted into the corresponding oxides by the removal from them of the elements of water, but that aldehydes or ketones are thus formed. For example, when ethylene glycol is heated with zinc chloride, acetaldehyde is formed,[1] and this is also produced when ethylene alcohol is heated with water to 220°—230°.[2]

[1] Wurtz, *Compt. Rend.* xlvii. 346 ; *Ann. Chem. Pharm.* cviii. 84.
[2] Nevolé, *Compt. Rend.* lxxxiii. 228.

In the case of the glycols richer in carbon the change takes place at a lower temperature, and it is not necessary first to prepare the glycols, inasmuch as if the dibromide of the olefine be heated with water and oxide of lead to 140°—150°, the glycols which are formed to begin with, decompose in various ways according to their constitution.[1] Thus compounds containing the group $-CHBr-CH_2Br$, form an aldehyde and a ketone, the glycol undergoing two distinct decompositions.

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ COH \end{array} + H_2O$$

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3. \end{array} + H_2O$$

If the group $=CBr-CH_2Br$ be present, the aldehyde only is formed; isobutylene dibromide, $(CH_3)_2CBr.CH_2Br$, yields isobutyl aldehyde $(CH_3)_2CH.COH$. If the compound contain the group $-CHBr.CBr.=$ or $=CBr.CBr=$ the ketone only is formed. Hence the pinacones decompose very readily into water and the ketones, to which the name of *pinacolines* is given. The formation of the ketones is seen in the following equations:

$$\begin{array}{l} CH_3\ CH_3 \\ \quad\diagdown\diagup \\ \quad C.OH \\ \quad | \\ \quad CH.OH \\ \quad | \\ \quad CH_3 \end{array} = \begin{array}{l} CH_3\ CH_3 \\ \quad\diagdown\diagup \\ \quad CH \\ \quad | \\ \quad CO \\ \quad | \\ \quad CH_3 \end{array} + H_2O$$

$$\begin{array}{l} CH_3\ CH_3 \\ \quad\diagdown\diagup \\ \quad C.OH \\ \quad | \\ \quad C.OH \\ \quad\diagup\diagdown \\ CH_3\ CH_3 \end{array} = \begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3-C-CH_3 \\ \quad\quad | \\ \quad\quad CO \\ \quad\quad | \\ \quad\quad CH_3. \end{array} + H_2O.$$

[1] Eltekow, *Journ. Russ. Chem. Ges.* x. 211.

458 *Ethereal Salts of the Dyad Radicals.* It has already been stated that the olefines readily combine with chlorine and bromine and, less easily, with iodine to form the haloid ethers, amongst which also ethereal salts are known, such as ethylene chloriodide, $C_2H_4ClI$, obtained by the union of ethylene and chlorine moniodide. Haloid ethers of dyad radicals are also formed by the action of chlorine or bromine on the chlorides or bromides of the monad radicals and these are, therefore, the second substitution-products of the paraffins. The compounds thus obtained are some of them identical with and others different from those obtained from the olefines. Thus, for instance, ethane yields ethidene chloride, $CH_3.CHCl_2$, isomeric with ethylene chloride, but propane yields propylene chloride, $CH_3.CHCl.CH_2Cl$ (Schorlemmer).

Bodies isomeric with the ethereal haloid salts are formed by the action of phosphorus pentachloride or phosphorus bromide on the aldehydes and ketones. Acetaldehyde or ethidene oxide yields ethidene chloride, and ordinary acetone, or dimethylmethylene oxide yields dimethylmethylene chloride, $CH_3\ CCl_2.CH_3$.

Other compounds may easily be obtained from the haloid ethers by double decomposition. As these reactions are analogous to those yielded by the haloid ethers of the monad radicals it is not necessary to enlarge on this subject here. Only one point must be mentioned, namely that the haloid ethers which are derived from aldehydes or ketones, cannot be converted into alcohols, although they can be converted into ethers or ethereal salts. Thus, for instance, aldehyde yields:

| Ethidene Diethyl Oxide. | Ethidene Diacetate. |
|---|---|
| $CH_3.CH(OC_2H_5)_2$ | $CH_3.CH(OC_2H_3O)_2$; |

but if we attempt to convert the last named body into the corresponding alcohol, aldehyde is again formed. It appears, however, not unlikely that ethidene alcohol and its homologues do exist in aqueous solution; for if aldehyde be mixed with water an evolution of heat, and contraction takes place, facts which seem to indicate the occurrence of the following reaction:

$$CH_3.CHO + H_2O = CH_3.CH(OH)_2.$$

This is rendered probable by another circumstance, namely that the aqueous solution of aldehyde boils higher than the pure compound (see part i. p. 477). As, however, water and aldehyde

may be completely separated by fractional distillation, or by means of calcium chloride, there is no doubt that ethidene alcohol, if it exists at all, must be a very unstable body.

Although alcohols containing two or more hydroxyls in contact with the same carbon atom have not been prepared in the pure state, the substitution-products of such compounds are known. Of these we have chloral hydrate, $CCl_3CH(OH)_2$, which has already been mentioned, and will hereafter be described as trichlorethidene glycol.

According to theory the compounds of the dyad radicals are more numerous than those of the monad ones, not only because in the first place a much larger number of cases of isomerism may occur, but also because, in addition to the simple compounds, that is those which contain two similar atoms or radicals, a large number of mixed compounds may exist in which two different atoms or radicals are present. Several examples of this kind have already been, and others will hereafter be, mentioned.

## MONOBASIC ACIDS OF THE SERIES $C_nH_{2n}O_3$.

459 It has already been stated that these monobasic acids, called the lactic series, from the long well known body lactic acid, are obtained by the moderate oxidation of those glycols containing an hydroxyl in the primary position. They may be more easily and simply obtained by replacing the halogen in the monosubstituted fatty acids by hydroxyl, and hence they are also termed the *hydroxy-* or *oxy-acids.* Thus for example, glycollic or oxyacetic acid is obtained by boiling an aqueous solution of a monochloracetate with an excess of water:

$$\begin{array}{l} CH_2Cl \\ | \\ CO_2H \end{array} + H_2O = \begin{array}{l} CH_2.OH \\ | \\ CO_2H \end{array} + HCl.$$

In a similar way *α*-monobrompropionic acid is converted into lactic acid:

α-Brompropionic Acid.

$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO_2H \end{array}$$

Lactic, or α-Oxypropionic Acid.

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO_2H. \end{array}$$

The acids of this group may also be obtained synthetically in a variety of ways:

(1) Their nitrils are formed by the direct combination of an aldehyde with hydrocyanic acid, and these are readily decomposed into the oxyacid by heating with a dilute mineral acid. Thus from acetaldehyde, lactic is prepared:

$$\begin{matrix}CH_3\\|\\CHO\end{matrix} + HCN = \begin{matrix}CH_3\\|\\CH.OH\\|\\CN.\end{matrix}$$

$$\begin{matrix}CH_3\\|\\CH.OH\\|\\CN\end{matrix} + 2H_2O + HCl = \begin{matrix}CH_3\\|\\CH.OH\\|\\CO.OH.\end{matrix} + NH_4Cl$$

(2) The ketones behave in an exactly similar way to the aldehydes. Thus acetone yields oxyisobutyric acid, $(CH_3)_2C(OH)CO_2H$, and this may also be easily obtained from monobrom-isobutyric acid.

(3) The nitrils of the oxyacids are also formed by heating the chlorhydrin with potassium cyanide. Ethylene chlorhydrin thus yields a nitril from which ethylene lactic acid can be obtained, a body isomeric with ordinary lactic acid or ethidene lactic acid:

Ethylene Cyanhydrate. Ethylene Lactic Acid.

$$\begin{matrix}CH_2.OH\\|\\CH\\|\\CN\end{matrix} \qquad \begin{matrix}CH_2.OH\\|\\CH_2\\|\\CO.OH.\end{matrix}$$

(4) Ethereal salts of the oxyacids are also formed when a normal ether of oxalic acid is treated with the zinc-compound of an alcohol-radical, or heated with zinc and the corresponding iodide, the product of the reaction being treated with water.[1] Thus for example the methyl ether of oxyisobutyric acid is obtained by the following reactions:

(*a*)
$$\begin{matrix}CO.OCH_3\\|\\CO.OCH_3\end{matrix} + Zn(CH_3)_2 = \begin{matrix}CH_3\ CH_3\\\diagdown\ \diagup\\CO.ZnOCH_3\\|\\CO.OCH_3.\end{matrix}$$

[1] Frankland and Duppa, *Proc. Roy. Soc.* xiii. 140.

$$(b)\quad \begin{matrix} CH_3\ CH_3 \\ \diagdown\ \diagup \\ CO.ZnOCH_3 \\ | \\ CO.OCH_3 \end{matrix} + 2H_2O = \begin{matrix} CH_3\ CH_3 \\ \diagdown\ \diagup \\ CO.H \\ | \\ CO.OCH_3 \end{matrix} + HO.CH_3 + Zn(OH)_2.$$

The oxyacids are at once alcohols and monobasic acids, and therefore exhibit the properties of both groups. When they are heated with the hydracids of the chlorine group their haloid ethers or monosubstituted fatty acids are formed:

$$\begin{matrix} CH_2.OH \\ | \\ CO_2H \end{matrix} + HBr = \begin{matrix} CH_2Br \\ | \\ CO_2H \end{matrix} + H_2O.$$

This reaction is in exact correspondence to that which occurs by the action of hydrobromic acid on alcohols. The moniodo-acids, formed in an analogous way, are reduced to fatty acids if a sufficient quantity of hydriodic acid be present:

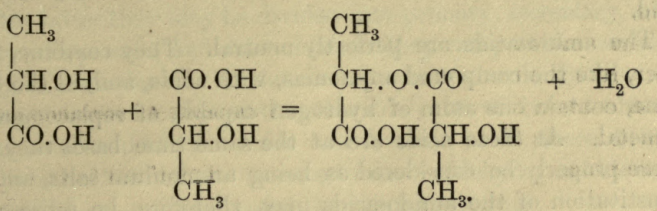
$$\begin{matrix} CH_2I \\ | \\ CO_2H \end{matrix} + HI = \begin{matrix} CH_3 \\ | \\ CO_2H \end{matrix} + I_2.$$

If lactic acid be heated with ethyl alcohol, ethyl lactate is obtained, a neutral liquid which is also an alcohol, and therefore contains one atom of hydrogen replaceable by sodium. If the sodium compound be treated with ethyl iodide diethyl lactate is formed, a neutral liquid which is decomposed by caustic potash with formation of potassium ethyl-lactate. From this salt ethyl-lactic acid itself can be obtained and this is isomeric with ethyl lactate, but differs from it widely, inasmuch as it is as powerful an acid as lactic acid itself. The constitution of these ethers and compound ethers is shown in the following formulæ:

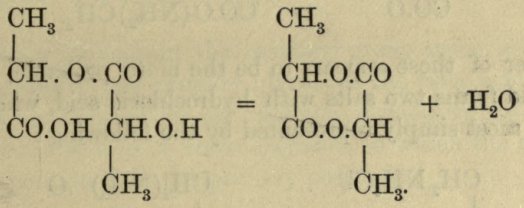
| Ethyl Lactate. | Diethyl Lactate. | Ethyl Lactic Acid. |
|---|---|---|
| $CH_3$ | $CH_3$ | $CH_3$ |
| \| | \| | \| |
| $CH.OH$ | $CH.OC_2H_5$ | $CH.OC_2H_5$ |
| \| | \| | \| |
| $CO.OC_2H_5$ | $CO.OC_2H_5$ | $CO.OH.$ |

As the acids of this group are at once alcohols and acids, they may unite with themselves to form ethers, two molecules acting upon one another, one acting as the acid and the other

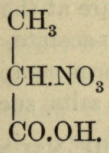
as the alcohol. On heating lactic acid the following reaction takes place:



The body thus obtained, is at once an ethereal salt, an alcohol and an acid, and on further heating, gives up water and is converted into a compound which is only an ethereal salt:

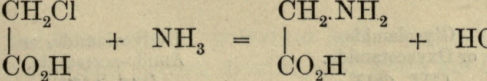


Concentrated nitric acid acts upon the oxyacids in a similar way as upon the alcohols, a nitric ether being formed. Lactic acid thus yields so-called nitro-lactic acid:



Heated with phosphorus pentachloride two hydroxyls of the acid are replaced by chlorine, compounds being formed which are at once alcoholic chlorides and acid chlorides. From lactic acid lactyl chloride, $CH_3.CHCl.COCl$, is obtained which on treatment with water is decomposed into hydrochloric acid and *a*-chlorpropionic acid.

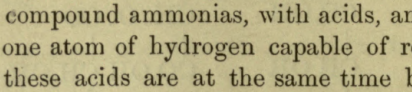
460 *The Amido-acids* are formed by the action of ammonia on the monosubstituted fatty acids. Thus chlorpropionic acid is converted into amidacetic acid:



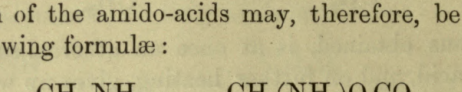
This reaction is analogous to that of the formation of the amines from the haloid ethers, and as in that case so also in this

the reaction easily passes beyond this point, diglycolamidic and triglycolamidic acids being formed together with glycolamidic acid.

The amido-acids are perfectly neutral. They combine, however, like the compound ammonias, with acids, and, at the same time, contain one atom of hydrogen capable of replacement by a metal. As these acids are at the same time bases they may more properly be considered as being ammonium salts, and the constitution of the amido-acids may, therefore, be represented by the following formulæ:

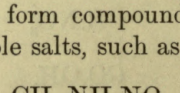


The latter of these appears to be the more probable, as amido-acetic acid forms two salts with hydrochloric acid, whose constitution is most simply represented by the following:



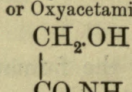
Metals which form powerful bases yield salts which have an alkaline reaction as they are at the same time amines; thus, for example, potassium amido-acetate, $CH_2(NH_2)CO_2K$.

The amido-acids also form compounds with salts, constituting a peculiar class of double salts, such as:

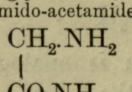


461 *Amides of the Oxyacids.* These bodies are isomeric with the amido-acids and are obtained in a similar way as the corresponding compounds of the fatty acid series. They act as weak bases but at the same time also as alcohols. If, on the other hand, the hydroxyl be replaced by the amido group, powerful bases are formed. Hence glycollic acid yields the following amido compounds:

Glycolamide, or Oxyacetamide.



Diglycolamide, or Amido-acetamide.



The above examples suffice to show the double character of the oxyacids. They are at once monobasic acids and alcohols. Like the latter they may be divided into primary, secondary, and tertiary compounds, and on oxidation they comport themselves exactly in a similar way to the corresponding simple alcohols.

It may also be mentioned that the aldehydes of these acids are known, as also aldehydic acids and ketonic acids, these being monobasic acids which at the same time are aldehydes or ketones. These will be mentioned under the special headings.

## DIBASIC ACIDS OF THE SERIES $C_nH_{2n-2}O_4$.

462 These acids contain the carboxyl group twice, and hence they are related to the primary glycols as the fatty acids are to the primary alcohols. They are therefore formed by oxidation of these glycols as well as of those oxyacids in which the alcoholic hydroxyl is contained in the primary position:

| Ethylene glycol. | Glycollic Acid. | Oxalic Acid. |
|---|---|---|
| $CH_2.OH$ | $CH_2.OH$ | $CO.OH$ |
| $\vert$ | $\vert$ | $\vert$ |
| $CH_2.OH.$ | $CO.OH.$ | $CO.OH.$ |

They can be prepared synthetically by a variety of methods.

(1) Their nitrils are formed when the haloid ethers of the olefines are heated with potassium cyanide. By the action of caustic potash or a mineral acid on these, the homologous acids are obtained of the series of which oxalic acid is the first term.

Ethylene can thus be easily converted into succinic acid:

| Succino-nitril. | | | Succinic Acid. | | |
|---|---|---|---|---|---|
| $CN$ | | | $CO.OH$ | | |
| $\vert$ | | | $\vert$ | | |
| $CH_2$ | | | $CH_2$ | | |
| $\vert$ | $+ 4H_2O$ | $=$ | $\vert$ | $+ 2NH_3$ | |
| $CH_2$ | | | $CH_2$ | | |
| $\vert$ | | | $\vert$ | | |
| $CN$ | | | $CO.OH.$ | | |

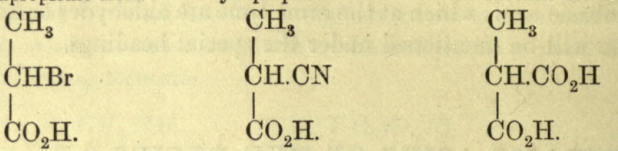
When a solution of the potasium salt of succinic acid is electrolysed, ethylene, carbon dioxide, and water are formed:

$$C_2H_4\begin{matrix}CO_2H\\CO_2H\end{matrix} = C_2H_4 + 2CO_2 + H_2.$$

The higher homologues are decomposed in an analogous way, the corresponding olefines being produced.

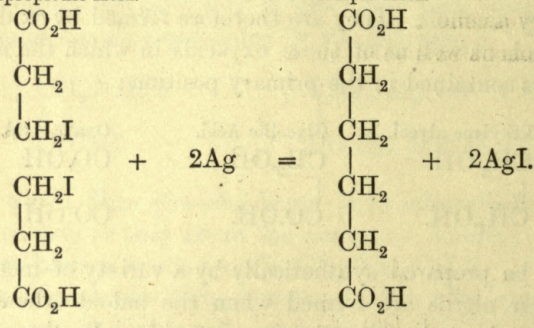
(2) The halogen in the monosubstituted fatty acids may be replaced by cyanogen, compounds being formed which are at once monobasic acids and nitrils, and these may be converted, by well known reactions, into the dibasic acids:

α-Brompropionic Acid. α-Cyanpropionic Acid. Iso-succinic Acid.



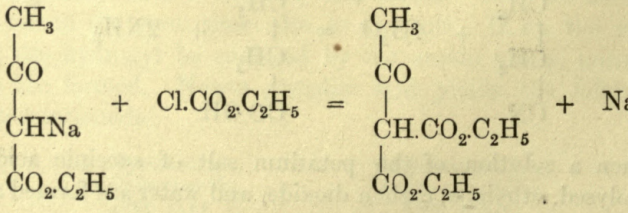
(3) The dibasic acids may also be obtained from the simple iodated fatty acids by heating with finely divided silver:

β-Iodpropionic Acid. Adipic Acid.



α-Brompropionic acid is converted by the same reaction into dimethyl-succinic acid, $CO_2H.CH(CH_3).CH(CH_3).CO_2H$.

(4) The synthetic preparation of these acids by means of the aceto-acetic ether reaction is of special importance, being capable, as the following examples show, of general applicability. By the action of ethyl chlorcarbonate on sodium aceto-acetic ether, *aceto-malonic ether* is obtained:



If ethyl monochloracetate be employed, the homologous *aceto-succinic ether* is produced; and the ethyl ether of

*a*-brompropionic acid yields the acetic ether of *pyrotartaric acid* or *methyl-succinic acid.* This latter ether is also obtained from sodium-methyl-aceto-acetic ether and ethyl chloracetate as well as when one atom of hydrogen in aceto-succinic ether is replaced by sodium and the compound thus obtained treated with methyl iodide.

Concentrated potash decomposes these ethers in a similar way to aceto-acetic ether:

$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CH_2 \\ | \\ CH.CO.CH_3 \\ | \\ CO.OC_2H_5 \end{array} + 3KOH = \begin{array}{l} CO.OK \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OK \end{array} + CH_3.CO.OK + 2HO.C_2H_5.$$

Diluted caustic potash or baryta-water on the other hand chiefly yields a ketonic acid:

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH—CO.OC_2H_5 \\ | \\ CH_2 \\ | \\ CO.OC_2H_5 \end{array} + 3KOH = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OK. \end{array} + CO(OK)_2 + 2HO.C_2H_5$$

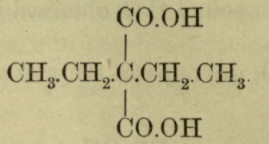
In this way *Methyl-ketone-propionic Acid,* or *a-Acetopropionic acid,* is produced.

(5) A no less important method is that in which *malonic acid,* $CH_2(CO_2H)_2$, is the starting point.[1] If the ethyl ether of this acid be treated with a solution of sodium ethylate, *sodium-malonic ether,* $CHNa(CO_2C_2H_5)_2$, is obtained, and in this the metal may easily be replaced by an alcohol radical when presented in the form of iodide:

$$\begin{array}{l} CO.OC_2H_5 \\ | \\ CHNa \\ | \\ CO.OC_2H_5 \end{array} + ICH_2.CH_3 = \begin{array}{l} CO.OC_2H_5 \\ | \\ CH.CH_2.CH_3 \\ | \\ CO.OC_2H_5 \end{array} + NaI.$$

[1] Conrad, *Ann. Chem. Pharm.* cciv. 127.

One atom of hydrogen in the ethyl-malonic ether thus formed can again be replaced by sodium, and the latter by an alcohol radical. If ethyl be again introduced, the ethyl ether of diethyl malonic acid is formed, an acid having the following constitution :



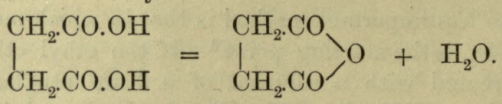
The salts and the free acid can readily be obtained from the ethyl ether.

The acids of the oxalic series, as they are named from their first term, can be prepared in many other ways, as by oxidizing the olefines with permanganic acid, when to begin with the fatty acids are formed, and then the methyl group converted into carboxyl.

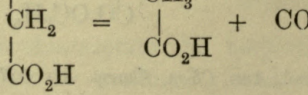
They are also obtained by oxidizing fatty acids with nitric acid, and, therefore, may be obtained from the monatomic alcohols and fats. Thus butyric acid yields succinic acid. In the case of the higher members of the series, the dibasic acid is easily further oxidized into one or more of its lower homologues.

The acids of the series $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$ are also converted by nitric acid into dibasic acids.

The acids of this group are solid at the ordinary temperature, more or less soluble in water, and when pure they crystallize well. At a higher temperature they decompose. Those which contain the two carboxyls connected with two different carbon atoms are resolved into an anhydride and water; thus succinic acid yields succinic anhydride :



Oxalic acid is an exception to this rule, as it, on heating, partly sublimes as unaltered acid and is partly decomposed into formic acid and carbon dioxide. An analogous decomposition occurs in the case of all the homologues, such as malonic acid, isosuccinic acid, &c., in which the carboxyls are linked to one carbon atom :



$$\begin{array}{l} CH_3 \\ | \\ CH{-}CO_2H \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CO_2H \end{array} + CO_2.$$

It is unnecessary to mention in detail the other chemical reactions of these acids. Being dibasic they form two series of ethers and of amido-compounds, as well as other compounds both simple and mixed. The following serve to illustrate this:

| Ethyl Oxalate. | Ethyl-oxalic Acid. | Ethyl-oxalyl Chloride. |
|---|---|---|
| $\begin{array}{l} CO.OC_2H_5 \\ \vert \\ CO.OC_2H_5. \end{array}$ | $\begin{array}{l} CO.OH \\ \vert \\ CO.OC_2H_5. \end{array}$ | $\begin{array}{l} COCl \\ \vert \\ CO.OC_2H_5. \end{array}$ |
| **Succinamide.** | **Succinamic Acid.** | **Succinimide.** |
| $C_2H_4\begin{array}{l}CO.NH_2 \\ CO.NH_2\end{array}$ | $C_2H_4\begin{array}{l}CO.OH \\ CO.NH_2\end{array}$ | $C_2H_4\begin{array}{l}CO \\ CO\end{array}NH.$ |

In each of the normal acids of this series, the melting-point decreases with every increase of $CH_2$ when the body contains an even number of carbon atoms. In the case of those containing uneven numbers, on the other hand, the melting-point of the acids increases with the increment $CH_2$, but it always remains lower than that of the acid next following which contains an even number of carbon atoms:

| | | M.P. |
|---|---|---|
| Succinic acid, | $C_4H_6O_4$ | 180° |
| Glutanic acid, | $C_5H_8O_4$ | 97 |
| Adipic acid, | $C_6H_{10}O_4$ | 148 |
| *a*-Pimelic acid, | $C_7H_{12}O_4$ | 100 |
| Suberic acid, | $C_8H_{14}O_4$ | 130 |
| *a*-Azelaic acid, | $C_9H_{16}O_4$ | 117 |
| Sebacic acid, | $C_{10}H_{18}O_4$ | 127 |
| Brassic acid, | $C_{11}H_{20}O_4$ | 108 |

It has however not yet been ascertained whether the two last named acids belong to the normal series.

## THE METHYLENE COMPOUNDS.

463 The radical *methylene* or *methene*, $CH_2$, appears incapable of existing in the free state. Various chemists have endeavoured to prepare it, but in vain. Perrot passed methyl chloride through a red-hot tube and obtained hydrochloric acid and ethylene together with other products.[1] Butlerow has moreover shown that it is not produced by the action of sodium or potassium on methylene iodide (di-iodomethane),[2] for on heating this latter compound with copper and water to 100° he obtained carbon monoxide, carbon dioxide, marsh gas, and ethylene, with some of its higher homologues.[3]

Hence it would appear that methylene in the nascent state combines with itself forming chiefly ethylene or dimethylene. This fact is a further confirmation of the conclusion that the hydrocarbons contain neither a dyad atom of carbon nor free combining units (see p. 5).

Although, however, the free radical methylene is unknown, many of its compounds have been prepared, of which some, such as the haloid ethers, &c., have already been described, being formed by the replacement of two atoms of hydrogen in methane by the elements of the chlorine group or by radicals (see part i. p. 253).

The oxide of methylene is formyl aldehyde, and, as has been stated, its aqueous solution probably contains methyl glycol, $CH(OH)_2$, a body not known in the free state, and probably not capable of a separate existence (part i. p. 268).

Of the other methyl compounds the following may be mentioned:

*Methylene Dimethyl Ether*, or *Methylal*, $CH_2(OCH_3)_2$, is formed together with formic acid and methyl formate, when wood-spirit is oxidized with manganese dioxide and dilute sulphuric acid.[4]

[1] *Ann. Chim. Phys.* [3], xlix. 94; *Ann. Chem. Pharm.* ci. 375.
[2] *Ann. Chem. Pharm.* cxi. 250. [3] *Ib.* cxx. 356.
[4] Malaguti, *Ann. Chim. Phys.* [2], lxx. 390; *Ann. Chem. Pharm.* xxxii. 55.

In order to explain the formation of this body, we may assume that the methyl alcohol is first oxidized to methylene glycol, and that this is then acted upon by the excess of wood-spirit as follows:

$$CH_2\begin{cases}OH\\OH\end{cases} + 2HO.CH_3 = CH_2\begin{cases}OCH_3\\OCH_3\end{cases} + 2H_2O.$$

Methylal is an aromatic smelling liquid boiling at 42°, and having at 18° a specific gravity of 0·855, that of its vapour being 2·625. It dissolves in three parts of water, and is converted, on further oxidation, into formic acid.

*Methylene Thiocyanate*, $CH_2(SCN)_2$, is formed by heating alcoholic solutions of methylene iodide and potassium thiocyanate. It crystallizes in fine prisms melting at 102°, and scarcely soluble in cold, though tolerably soluble in boiling water, and imparting to steam a pungent smell, the vapours acting violently on the mucous membrane. Nitric acid oxidizes it to methylene disulphonic acid (see part i. p. 264).

*Methylene Acetate*, $CH_2(OC_2H_3O)_2$, is formed by heating methylene iodide with silver acetate. It is an oily liquid boiling about 170°, and having a strong aromatic pungent taste and smell. When heated with water to 100° it is converted into acetic acid and paraformaldehyde.[1]

*Methylene Aceto-methyl-Oxide*, $CH_2\begin{cases}OCH_3\\OC_2H_3O\end{cases}$. Monochlorinated methyl oxide may be regarded as the methyl ether of the unknown methylene chlorhydrin. It is easily decomposed by potassium acetate as follows:

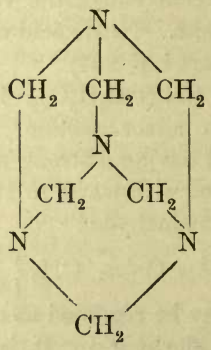
$$CH_2\begin{cases}OCH_3\\Cl\end{cases} + KO.C_2H_3O = CH_2\begin{cases}OCH_3\\OC_2H_3O\end{cases} + KCl.$$

The acetate thus obtained is a liquid boiling at 117°—118°.[2]

*Methylene Acetochloride*, or *Methylene Chloracetin*, $CH_2\begin{cases}Cl\\OC_2H_3O\end{cases}$, is the first product of the action of chlorine on methyl acetate. It is a mobile liquid possessing a suffocating pungent smell, and a burning taste It boils at 115°—116°, and at 14° has a specific gravity of 1·1953, and is converted on heating with sodium acetate into methylene acetate.[3]

[1] Butlerow, *Ann. Chem. Pharm.* cvii. 111; cxi. 245.
[2] Friedel, *Compt. Rend.* lxxxiv. 247.
[3] Henry, *Ber. Deutsch. Chem. Ges.* vi. 739.

464 *Hexmethylenamine*, $(CH_2)_6N_4$, was prepared by Butlerow[1] by acting with dry ammonia on paraformaldehyde. It is also formed in an analogous way from monochlormethyl oxide and other methylene compounds. It is easily soluble in water, and with difficulty in cold alcohol, crystallizing from hot saturated solution in glistening rhombohedrons or short prisms which begin to sublime at 100°, evolving an unpleasant smell like mice and salt-fish. Hexmethylenamine has an alkaline reaction and is a monacid amine. Its salts crystallize in long needles and yield the compound $(C_6H_{12}N_4,ClH)_2PtCl_4$ with platinum chloride, which is almost insoluble in water. Hexmethylenamine is formed by the replacement in two molecules of paraformaldehyde or trioxymethylene of six atoms of oxygen by four atoms of nitrogen. It has, therefore, probably the following constitution :




By the action of ethylamine on methylene oxide a base is formed having the composition $N_2(CH_2)_2(C_2H_5)_2$ or $N_4(CH_2)_4(C_2H_5)_4$. It is an oily liquid whose salts do not crystallize, and even the platinichloride which has the composition $2N_2(CH_2)_2(C_2H_5)_2HCl+PtCl_4$, is uncrystallizable.

If methylene iodide be heated with triethylamine to 100° an iodide, $N(C_2H_5)_3(CH_2I)I$, is formed, crystallizing in fine tetragonal tables. That the compound has the above constitution is proved by the fact that silver acetate only removes one half of the iodine. When its solution is treated with silver chloride, and platinic chloride added to the evaporated liquid, the tolerably soluble salt $2N(C_2H_5)_3(CH_2I)Cl+PtCl_4$ is formed, crystallizing in splendid octohedrons. The free base is not known.[2]

[1] *Ann. Chem. Pharm.* cxv. 322 ; Hofmann, *Ber. Deutsch. Chem. Ges.* ii. 153.
[2] Julie Lermontoff, *Ber. Deutsch. Chem. Ges.* vii. 1252.

# THE ETHYLENE COMPOUNDS.

## ETHYLENE, $C_2H_4$.

465 Becher appears to have been the first to observe that a combustible vapour is given off by the action of sulphuric acid upon alcohol. In his *Physica subterranea* he says: "*Evidens demonstratio ignis est in spiritu vini et oleo vitrioli, utroque probe rectificato. Quam primum enim confunduntur, ignem concipiunt, qui vase obstructo extinguitur, aperto rursus incenditur.*"

These remarks can only apply to a combustible gas, or to the vapour of ether; and, although he does not mention it, there can be little doubt that there was a flame in the neighbourhood.

The next information we possess concerning a combustible gas produced in this way, is given by Ingenhouss,[1] who states that he saw such a gas evolved in the house of a certain Enée in Amsterdam. It was then considered to be identical with the so-called inflammable air, and was thought to be a good kind of this air, because when burnt with ordinary air it exploded so violently. This view was held by Deimann and Paets van Troostwyk in 1781, who together with Bondt and Lauwerenburgh examined the properties of this gas more thoroughly in 1795. They showed that it consists only of carbon and hydrogen and approximately determined its specific gravity.[2] They found that it unites with chlorine, yielding an oily compound, and they named it *gas huileux*, a designation which was afterwards changed by Fourçroy to olefiant gas.

That this body is a substance differing from marsh gas, was first shown by W. Henry of Manchester, and his view was soon supported by the investigations of Dalton, Humphry Davy, Berzelius, and others.

[1] Priestley, *Observations and Experiments Relating to Various Branches of Natural Philosophy*, i. 1779.

[2] *Crell. Ann.* 1795, 2, 195, 310 and 430.

As these two were the only hydrocarbons known at that time they were distinguished as *light* and *heavy carburetted hydrogen*, whilst Berzelius gave to the latter the name of *Elayl*, as it plays the part of a compound radical.

It has already been stated in the introduction to the organic portion of this treatise that for some time a belief prevailed that the laws of combination in constant and multiple proportion do not hold good in the case of organic compounds, and hence it appears remarkable that it was by the investigation of the composition of two organic bodies, namely marsh gas and olefiant gas, that Dalton was led to the establishment of these very laws, and thence to his atomic theory.

The four Dutch chemists above named prepared ethylene by heating strong alcohol with three to four parts of sulphuric acid. In this case, a tolerably pure gas is evolved to begin with, mixed, however, with the vapour of alcohol and ether, which impurities can be removed by passing the gas through concentrated sulphuric acid.[1] It may also contain carbon dioxide mixed with it, and this may be easily removed by caustic potash. At a later period of the decomposition sulphur dioxide and carbon monoxide,[2] and probably also marsh gas,[3] are given off, the black mass frothing strongly and passing out of the flask. In order to prevent this, at Wöhler's [4] suggestion, sand is added to the liquid until a thick pasty mass is obtained, but this leaves a hard residue which cannot be removed from the vessel without breaking it. To avoid this, and to obtain a pure gas, many other suggestions have been made. Thus some time ago Magnus [5] suggested that one part of spirit of wine and sixteen parts of sulphuric acid should be heated, and as soon as the mass becomes black a further addition of alcohol should gradually be made. According to Mitscherlich [6] a mixture of three parts of water and ten parts of sulphuric acid is heated to its boiling point, which lies about 160°—165°, and the vapour of eighty per cent. alcohol led in at this temperature. The gas, which is then quietly evolved, only contains as impurities the vapours of water, alcohol, and ether.

The method now generally adopted is that suggested by Erlenmeyer and Bunte,[7] or rather the improved process suggested afterwards by Erlenmeyer.[8] A mixture of 25 grams of alcohol

[1] Liebig, *Ann. Pharm.* xiv. 150.
[2] Vogel, *Journ. Prakt. Chem.* xxv 300.
[3] Faraday, *Bibl. Univ.* lix. 114.
[4] *Ann. Chem. Pharm.* xci. 127.
[5] *Pogg. Ann.* xlvii. 524.
[6] *Ann. Chim. Phys.* [3], vii 12.
[7] *Ann. Chem. Pharm.* clxviii. 64.
[8] *Ib.* cxcii. 244.

and 150 grams of sulphuric acid is brought into a flask (Fig. 99) of two to three liters capacity, and this heated until a rapid evolution of gas occurs, and at this point a mixture of one part of alcohol and two parts of sulphuric acid is allowed to drop in, the gas which is evolved being washed through sulphuric acid and then through caustic soda.

Gladstone and Tribe found that when their copper-zinc couple is brought in contact with ethylene bromide and water, pure ethylene is given off, and in presence of alcohol this reaction is brought about by zinc alone.[1] This last reaction may be used

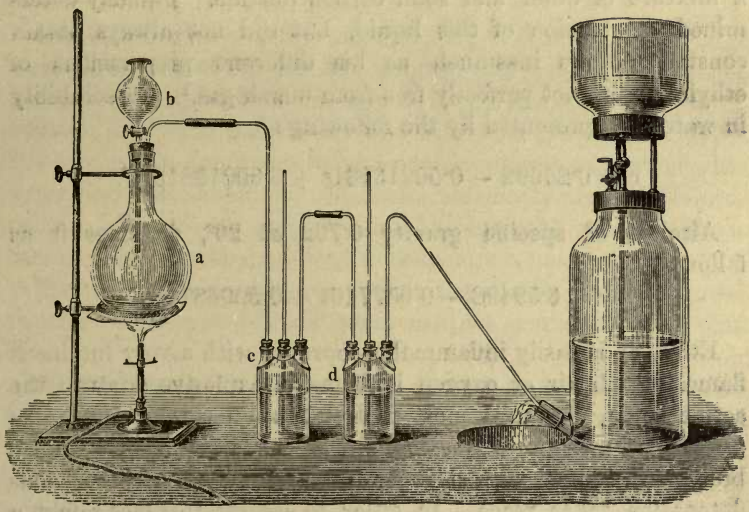



Fig. 99.

for lecture purposes for the quick preparation of small quantities of ethylene, but the decomposition must be assisted by heat.[2]

It has already been stated that ethylene is formed, together with its homologues, in the dry distillation of many organic bodies, and coal gas contains on an average from four to five per cent.

The formation of ethylene, according to a method pointed out by Tollens, viz. that of heating ethidene chloride, $CH_3.CHCl_2$,

[1] *Journ. Chem. Soc.* 1874, 406.

[2] Sabanejew, *Journ. Russ. Chem. Ges* ix 33; *Ber. Deutsch. Chem. Ges.* ix. 1810.

with sodium, is of interest. And its production from acetylene, $C_2H_2$, a body which can itself be obtained by direct union of its elements, is of importance as being the first step in the synthesis of alcohol. Acetylene combines with nascent hydrogen to form ethylene, and this latter is also formed when di-iodmethane is treated with water and copper, or methyl chloride passed through a red-hot tube.

466 *Properties.* Ethylene is a colourless gas, possessing a faint but peculiar and rather suffocating odour and having a specific gravity of 0·9709 (Th. Thomson). It may be condensed to a liquid either by means of pressure or by cooling it down to −110° in a mixture of ether and solid carbon dioxide. Faraday determined the tension of this liquid, but did not always obtain constant results inasmuch as his different preparations of ethylene were not perfectly free from marsh gas.[1] Its solubility in water is represented by the following: [2]

$$c = 0{\cdot}25692 - 0{\cdot}00913631t + 0{\cdot}000188108t^2.$$

Alcohol, of specific gravity 0·792 at 20°, dissolves it as follows:

$$c = 3{\cdot}59498 - 0{\cdot}057716t + 0{\cdot}0006812t^2.$$

Ethylene is easily inflammable, burning with a very luminous flame. With air or oxygen it forms an explosive mixture, the action being, of course, most powerful when three volumes of oxygen are present to one volume of the gas. If ethylene be brought in contact with strongly ozonized oxygen, a spontaneous detonation takes place. In order to exhibit this fact safely, a current of the hydrocarbon is led through a tube 10mm. in diameter whilst ozonized air is allowed to pass through a narrow tube which passes to the depth of 1 cm. inside the wide one. Each bubble produces an explosion which is usually accompanied by the formation of a white vapour.[3] Fuming nitric acid easily oxidizes ethylene to oxalic acid. Chromic acid solution converts it at once into aldehyde,[4] the ethylene first combining with water to form ethyl alcohol, and this undergoing oxidation. The process may be carried on further, acetic acid, and oxalic acid, together with carbon dioxide and formic acid, being produced.[5] Concen-

[1] *Loc. cit.* [2] Bunsen, *Gasometry*, 150, 152.
[3] Houzeau and Renard, *Compt. Rend.* lxxvi. 572.
[4] Berthelot, *Compt. Rend.* lxviii. 334; *Ann. Chem. Pharm.* cl. 373.
[5] O. and F. Zeidler, *Ann. Chem. Pharm.* cxcvii. 246.

trated sulphuric acid absorbs ethylene with formation of ethyl sulphuric acid (Faraday, Hennel; see part i. p. 296), combination taking place quickly if the two bodies be shaken together, and still more easily if the ethylene is passed into sulphuric acid heated to 160°—170°.[1]

Ethylene combines with chlorsulphonic acid to form ethyl chlorosulphate. If it be heated for some time with hydriodic or hydrobromic acid to 100°, the corresponding ethyl-haloid ether is formed, but no combination takes place under these circumstances with hydrochloric acid.[2]

Ethylene also combines with hydrogen, in the presence of platinum black, to form ethane.[3]

467 *Ethylene Boron Fluoride*, $C_2H_4BF_3$, is formed when a mixture of ethylene and boron fluoride, warmed to a temperature of 25°—30°, is exposed to sunlight. It is a fuming liquid which boils at 124°—125°, and at 23° has a specific gravity of 1·0478. It burns with a fine green flame and decomposes on contact with water into boric acid and a volatile pleasantly smelling liquid, boiling between 10° and 15°, and burning with a bright green flame. This is probably ethyl fluoride.[4]

The existence of ethylene boron fluoride is a further proof that in certain compounds boron can act as a pentad element (part i. p. 448).

*Ethylene Ferrous Chloride*, $C_2H_4FeCl_2+2H_2O$, is formed when an ethereal solution of ferric chloride is heated for some hours to 140°—150°, and the compound is more easily obtained if, at the same time, a solution of phosphorus in bisulphide of carbon is added. It forms flat colourless scales or prisms which are easily soluble in water.[5]

The corresponding bromide, $C_2H_4FeBr_2+2H_2O$, is produced by passing ethylene in the sunlight into a concentrated aqueous solution of ferrous bromide, when pale green very deliquescent crystals are deposited.[6]

*Ethylene Platinous Chloride*, $C_2H_4PtCl_2$, was discovered by Zeise [7] in 1831, and termed inflammable chloride of platinum. It is obtained by boiling alcohol with platinic chloride and

[1] Berthelot, *Ann. Chim. Phys.* [3], xliii. 385.
[2] Berthelot, *Compt. Rend.* xliv. 1350; l. 612; *Ann. Chem. Pharm.* civ. 184; cxv. 114.
[3] Wilde, *Ber. Deutsch. Chem. Ges.* vii. 354.
[4] Landolph, *Ber. Deutsch. Chem. Ges.* xii. 1586.
[5] Kachler, *Ber. Deutsch. Chem. Ges.* ii. 510.
[6] Chojnacki, *Zeitsch. Chem.* 1870, 420.
[7] Zeise, *Pogg. Ann.* xxi. 497, 542; xl. 234.

evaporating in a vacuum. Its formation, leaving out the by-products, is shown in the following equation (Birnbaum):

$$PtCl_4 + 2C_2H_6O = C_2H_4PtCl_2 + C_2H_4O + H_2O + 2HCl.$$

It is also formed when ethylene is passed through a hydrochloric acid solution of platinous chloride.[1]

It is a light lemon yellow powder difficultly soluble in water, and when heated it burns rapidly. When warmed with an excess of caustic potash it is converted into a black powder which when dry explodes on heating. From its solution and that of its double salts, ammonia precipitates a bright yellow unstable compound, consisting of $C_2H_4PtCl_2$, $NH_3$, which unites with hydrochloric acid to form *ethyl platinous ammonium chloride* or *detonating chloride of platinum*, $C_2H_4PtCl_2$, $NH_4Cl+H_2O$, a body crystallizing from water in lemon-yellow oblique rhombic prisms and obtained easily by the direct combination of sal-ammoniac with ethylene platinous chloride. This substance serves for the preparation of ethylene platinous chloride in the pure state. For this purpose a concentrated solution of platinic chloride is added to a concentrated solution of ethylene platinous ammonium chloride so long as a precipitate of ammonium platinichloride is formed, and the filtrate evaporated in a vacuum over sulphuric acid.

*Ethylene Platinous Potassium Chloride*, $C_2H_4PtCl_2KCl + H_2O$. This resembles the ammonium salt, and decomposes at about 200°, with evolution of ethylene.

The references at the foot may be consulted for further information respecting these platinum ethylene compounds.[2]

## ETHYLENE ALCOHOL, OR ETHYLENE GLYCOL, $C_2H_4(OH)_2$.

468 This alcohol is the first member of the group of alcohols containing dyad radicals. It was discovered by Wurtz in 1856 (see p. 9). He obtained it by treating ethylene di-iodide with silver acetate, and decomposing the ethylene diacetate thus obtained with caustic potash.[3] He afterwards employed ethylene

[1] Birnbaum, *Ann. Chem. Pharm.* cxlv. 67.

[2] Martius and Griess, *Ann. Chem. Pharm.* cxx. 326; Chojnacki, *loc. cit.*; Schützenberger and Fontaine, *Bull. Soc. Chim.* xviii. 103; Sadtler, *ib.* xvii. 54.

[3] *Compt. Rend.* xliii. 199; *Ann. Chem. Pharm.* c. 110.

dibromide, a body more readily obtained, and he decomposed the acetic ether with caustic baryta.[1]

Atkinson then found that when potassium acetate is heated in closed vessels to 100° with ethylene bromide and alcohol until no further potassium bromide separates out, the mono-acetate is obtained according to the following equation: [2]

$$C_2H_4\begin{cases}Br\\Br\end{cases} + 2\,\begin{matrix}C_2H_3O\\K\end{matrix}\Big\}O + \begin{matrix}C_2H_5\\H\end{matrix}\Big\}O =$$

$$C_2H_4\begin{cases}OH\\OC_2H_3O\end{cases} + \begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\Big\}O + 2KBr.$$

This decomposition also occurs when the mixture is heated in a flask with a reversed condenser.[3]

The mono-acetate is afterwards converted into glycol either by treatment with caustic baryta, or by heating with water in closed tubes.[4]

According to Erlenmeyer a mixture of 600 grams of ethylene dibromide, 700 grams of fused potassium acetate and 1500—1800 of alcohol of specific gravity 0·83, is boiled in connection with a reversed condenser until the liquid does not precipitate ethylene dibromide on the addition of water. The well-cooled liquid is then placed on a vacuum-filter to remove the potassium bromide, and the filtrate submitted to distillation. The portion passing over above 140° is treated with an excess of caustic baryta dissolved in the necessary quantity of water, and then heated for twelve hours on the water-bath. The free baryta is next precipitated by carbon dioxide, and the filtrate evaporated on a water-bath to one-third. The residue is then treated with a mixture of equal parts of strong alcohol and ether, and the liquid poured off from the saline mass which is deposited, the residue being thrown on to the filter and washed with alcohol and ether. The solutions, which are now mixed together, are distilled on a water-bath so as to separate alcohol and ether, and the residual liquid subjected to fractional distillation. The portion coming over below 186° is afterwards concentrated on the water-bath, and the residue, united with the higher portions, yields pure glycol on further distillation.[5] If strong alcohol be used, and only half the theoretical quantity of potassium acetate, no monacetate is formed,

[1] *Ann. Chim. Phys.* [3], lv. 400.
[2] *Phil. Mag.* [4], xvi. 433; *Ann. Chem. Pharm.* cix. 232.
[3] M. Simpson, *Proc. Roy. Soc.* ix. 725.
[4] Debus, *Ann. Chem. Pharm.* cx. 316.
[5] Erlenmeyer, *Ann. Chem. Pharm.* cxcii. 244.

according to Demole, but glycol itself, and this may then be separated from the unattacked ethylene bromide by distillation.[1] This mode of preparation has given discrepant results in the hands of different experimenters,[2] and the conditions under which the largest yield is obtained have not been determined.[3]

According to Hüfner and Zeller,[4] glycol is obtained readily by boiling 138 grams of pure potassium carbonate with 188 grams of ethylene bromide dissolved in one liter of water, with a reversed condenser, when the following reaction takes place :

$$C_2H_4Br_2 + H_2O + CO(OK)_2 = C_2H_4(OH)_2 + 2KBr + CO_2.$$

The solution is then concentrated on a water-bath, and after cooling poured off from the deposited potassium bromide, the crystals being brought on to a filter pump and washed with absolute alcohol. From the united solutions the ethylene alcohol is separated by fractional distillation. In this preparation a certain loss takes place from the formation of monobromethylene, $C_2H_3Br$, and here, too, the conditions of best yield have as yet not been exactly worked out.[5]

Ethylene bromide may also be converted into glycol by heating it to 170° in contact with water and oxide of lead.[6] The lead oxide may be omitted if sufficient water be added to prevent the formation of concentrated hydrobromic acid, and this reaction takes place, though slowly, at 140°—150°.[7]

Ethylene alcohol is also formed when a solution of hydrogen dioxide is allowed to remain for some time in contact with ethylene.[8]

469 *Properties.* Glycol is a colourless liquid having the consistency of a thin syrup, and possessing no smell but having a sweet taste. It boils at 197°–197°·5, and at 0° has a specific gravity of 1·125, that of its vapour being according to Wurtz 2·164 at 292°. Ethylene glycol is miscible with water and alcohol in all proportions, but is not soluble in ether. It dissolves

[1] Demole, *Ann. Chem. Pharm.* clxxiii. 117 ; clxxvii. 45.
[2] Zeller, *Journ. Prakt. Chem.* [2], x. 286 ; Börnstein, *Ber. Deutsch. Chem. Ges.* ix. 480 and 917.
[3] Erlenmeyer, *loc. cit.*
[4] *Journ. Prakt. Chem.* [2], x. 270 ; xi. 229.
[5] Lietzenmayer, *Ann. Chem. Pharm.* clxxx. 282 ; Stempnewsky, *ib.* cxcii. 240 ; Erlenmeyer, *loc. cit.*
[6] Jeltekow, *Ber. Deutsch. Chem. Ges.* vi. 558.
[7] Niederist, *Ann. Chem. Pharm.* clxxxvi. 393.
[8] Carius, *Ann. Chem. Pharm.* cxxvi. 195.

various salts in small quantities, especially chlorides, and also potassium carbonate, caustic potash, and lime.

Oxidizing agents convert it into glycollic acid, $CH_2(OH).CO_2H$; glyoxylic acid, $CH(OH)_2.CO_2H$; and oxalic acid, $CO_2H.CO_2H$.

When glycol is heated with zinc chloride, acetaldehyde and crotonaldehyde, $C_4H_6O$, are formed together with other products; acetaldehyde is also formed when ethylene glycol is heated with water to 220°–230°.[1]

*Sodium Mono-ethylenate*, $C_2H_4(OH)ONa$, is a white crystalline body obtained by the action of sodium on glycol. When heated with sodium in an oil-bath to 190°, *disodium ethylenate*, $C_2H_4(ONa)_2$, is formed.

*Ethylene Ethyl Ether*, $C_2H_4(OH)OC_2H_5$, is formed by treating the mono-sodium compound with ethyl iodide. It has however not been obtained in the pure state, as some disodium ethylenate is at first formed. It is a very pleasantly smelling liquid boiling at 127°.

*Ethylene Diethyl Ether*, $C_2H_4(OC_2H_5)_2$, is readily obtained when the foregoing compound is treated with one-fourth its weight of potassium, and the cold mass warmed with ethyl iodide. The whole is then distilled, and again rectified over potassium. This compound is a pleasantly ethereal-smelling liquid boiling at 123°·5, and having a specific gravity at 0° of 0·7993.[2]

## ETHYLENE OXIDE, $C_2H_4O$.

**470** This interesting compound was also discovered by Wurtz.[3] It is formed directly from glycol by the withdrawal of the elements of water. In order to prepare it concentrated caustic potash must be gradually added to ethylene chlorhydrin, when a violent reaction at once occurs, but after a time the reaction must be aided by heat:

$$\begin{matrix} CH_2Cl \\ | \\ CH_2OH \end{matrix} + KOH = \begin{matrix} CH_2 \\ | \quad O \\ CH_2 \end{matrix} + KCl + H_2O.$$

[1] Nevolé, *Compt. Rend.* lxxxiii. 228.
[2] Wurtz, *Ann. Chim. Phys.* [3], lv. 400; *Ann. Chem. Pharm.* cviii. 84.
[3] *Comptes Rendus*, xlviii. 101; *Ann. Chem. Pharm.* cx. 125.

Ethylene oxide is evolved as a gas, which is first passed through a tube filled with chloride of calcium, and then into a well-cooled receiver, where it condenses. In order to prepare it perfectly pure it must be allowed to stand over calcium chloride and afterwards be rectified.

Ethylene oxide is a pleasantly smelling ethereal liquid boiling at 13°·5, and at 0° having a specific gravity of 0·8945, whilst that of the vapour is 1·422. It mixes with water, alcohol and ether, in every proportion. When sodium amalgam is added to its aqueous solution it is reduced to ethyl alcohol.[1] Although it possesses a neutral reaction it acts as a very strong base, and hence forms "a link between organic and mineral chemistry."[2] Thus for example, it unites so easily with hydrochloric acid to form ethylene chlorhydrate that when equal volumes of the gases are brought together over mercury, the combination takes place as quickly as between hydrochloric acid and ammonia. It unites with acetic acid directly, forming, according to the quantity added, either monacetate or diacetate. Brought in contact with magnesium chloride, it yields a precipitate of magnesia which forms slowly in the cold but quickly when warmed:

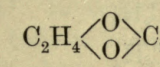
$$2C_2H_4O + 2H_2O + MgCl_2 = 2C_2H_4\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + Mg(OH)_2.$$

It acts in a similar way with the salts of copper, iron, aluminium, &c.[3]

471 *Diethylene Dioxide*, $(C_2H_4)_2O_2$. If ethylene oxide be brought in contact with well-cooled bromine, and if the mixture be allowed to remain in a freezing mixture for a day, orange-yellow or ruby-red prisms separate out, possessing the composition $(C_2H_4O)_2Br_2$. These melt at 65°, and are again formed on cooling. The constitution of this singular compound has not as yet been satisfactorily ascertained. It contains bromine only loosely combined, as it gradually parts with this element in the cold in contact with mercury, when, instead of ethylene oxide being formed, the bimolecular compound is set free. This is a pleasant but faintly-smelling liquid, boiling at 102°, and having a specific gravity at 0° of 1·0482, whilst that of its vapour is 3·10. On cooling, it solidifies to a crystalline mass, melting at 9°.[4]

[1] Wurtz, *Comptes Rendus*, liv. 277; *Ann. Chem. Pharm.* cxxii. 354.
[2] Wurtz, *Journ. Chem. Soc.* xv. 387.
[3] *Comptes Rendus*, l. 1195; *Ann. Chem. Pharm.* cxvi. 249.
[4] *Comptes Rendus*, liv. 277; *Ann. Chem. Pharm.* cxxii 354.

Diethylene dioxide has doubtless the following constitution :

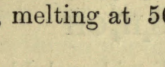
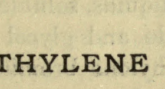
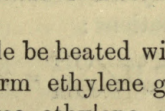
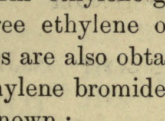


*Para-ethylene Oxide.* Ethylene oxide on standing for some time is converted into a polymeric modification, which is a white crystalline mass, melting at 56°.[1]

## POLYETHYLENE ALCOHOLS.

472 If ethylene oxide be heated with water to 100° these substances combine to form ethylene glycol, and this, in its turn, combines with the free ethylene oxide to form polyethylene alcohols. These bodies are also obtained by heating glycol with ethylene oxide[2] or ethylene bromide.[3]

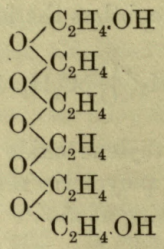
The following are known :

| | | B.P. |
|---|---|---|
| Diethylene alcohol, |  | 250° |
| Triethylene alcohol, |  | 290° |
| Tetrethylene alcohol, |  | 230° under a pressure of 25 mm. |
| Pentethylene alcohol, |  | 281° „ „ |

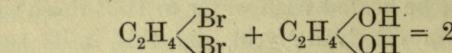
[1] *Compt. Rend.* lxxxiii. 1141.

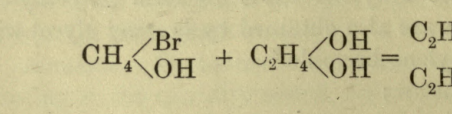
[2] Wurtz, *Compt. Rend.* xlix. 813 ; l. 1195 ; *Ann. Chem. Pharm.* cxiii. 255 ; cxvi. 249.

[3] Lourenço, *Ann. Chem. Pharm.* cxvii 269 ; *Ann. Chim. Phys.* [3], lxvii. 288.

Hexethylene alcohol,  325° under a pressure of 25 mm.

These are all thick, viscid liquids, soluble in water. Their production from ethylene oxide and glycol is readily understood, and their formation from ethylene bromide and glycol is represented by the following equations:





Polyethylene alcohols are also formed when glycol is heated with ethylene chlorhydrin, this reaction taking place at about 120°. When heated more strongly, the chlorhydrins or bromhydrins of the polyethylene alcohols are formed. The ethers of these same alcohols are produced by heating ethylene oxide with the acids or anhydrides.

## ETHEREAL SALTS OF ETHYLENE.

473 The number of these is very large, as not only one or both of the hydroxyls in glycol can be replaced, but two different radicals may be introduced.

*Ethylene Chlorhydrin*, or *Chlorhydrate*, $C_2H_4Cl(OH)$. This compound was first obtained by Wurtz by saturating ethylene alcohol at the ordinary temperature with hydrochloric acid gas and then heating the solution in closed tubes to 100°, operations which must be several times repeated in order to convert the glycol completely into chlorhydrin. The product is then treated with potassium carbonate and purified by fractional distillation.[1] It is also formed when glycol is warmed with sulphur monochloride:[2]

$$2C_2H_4(OH)_2 + 2S_2Cl_2 = 2C_2H_4Cl(OH) + 2HCl + SO_2 + 3S.$$

[1] *Ann. Chim. Phys.* [3], lv. 400; *Ann. Chem. Pharm.* cx. 125.
[2] Carius, *Ann. Chem. Pharm.* cxxvi. 195.

It is likewise produced by the direct combination of ethylene and hypochlorous acid.[1] In order to prepare it according to this reaction, a large balloon is filled with olefiant gas, and the hypochlorous acid obtained from 6 grams of mercuric oxide added for every 1 liter of the gas. This is then allowed to stand for some days and the liquid diluted with water, any hypochlorous acid which may be present being destroyed by the addition of sodium thiosulphate. The liquid is then distilled until the distillate ceases to have a sweet taste, saturated with sodium chloride, and the chlorhydrin removed from the liquid by shaking with ether.[2]

Ethylene chlorhydrin is a colourless, sweet-tasting liquid, boiling at 128°, its vapour having a density of 2·797. When brought in contact with water and sodium amalgam it is converted into ethyl alcohol, and it yields chloracetic acid on oxidation. Hence it may be regarded as *monochlor-ethyl-alcohol.*

*Ethylene Dichloride,* $C_2H_4Cl_2$. This compound is known, from its discoverers, as *Dutch liquid.* It is easily formed when ethylene and chlorine are brought together, but the combination takes place slowly, inasmuch as the double linkage of the carbon has first to be replaced by single linkage. If one volume of ethylene and two volumes of chlorine are equally mixed and the whole ignited, a deep red flame passes through the mixture, hydrochloric acid is formed and thick clouds of soot are deposited (Deiman, &c.).

At the time of the discovery of Dutch liquid, chlorine was considered to be oxidized muriatic acid, and hence it was assumed that in the formation of the oil the oxygen united with the hydrocarbon, and the product was looked upon as a body resembling some of the fatty oils. It was recognized by Colin and Robiquet[3] to be analogous to hydrochloric ether (ethyl chloride), and its composition was afterwards determined by Liebig,[4] Dumas,[5] and Regnault,[6] who investigated the compound more closely.

[1] Carius, *ib.* cxxiv. 257.

[2] Butlerow, *Ann. Chem. Pharm.* cxliv. 40. The solution of hypochlorous acid must be prepared from moist, freshly-precipitated mercuric oxide, in which the amount of dry oxide must be determined. To four grams of the latter so much water and ice is added that 15 parts of the mixture contain one part of dry oxide. This is then saturated in the dark with chlorine gas, and afterwards half as much moist oxide added, and the mixture used directly.

[3] *Ann. Chim. Phys.* [2], i. 337.

[4] *Ann. Pharm.* i. 213; ix. 20.

[5] *Ann. Chim. Phys.* xlviii. 185; lvi. 145.

[6] *Ib.* lviii. 301; lxix. 151.

In order to show the formation of Dutch liquid, the apparatus employed by Colin and Robiquet and since improved upon may be used. In the tubulated balloon (Fig. 100) equal volumes of dry ethylene and chlorine are brought. The ethylene dichloride which is formed condenses on the sides of the glass and falls into the flask, which is kept cool by water, as heat is of course evolved during the reaction.

In order to obtain larger quantities of ethylene dichloride, Limpricht's method may be employed. For this purpose ethylene is passed into a slightly-warmed mixture of 2 parts of manganese dioxide, 3 parts of common salt, 4 parts of water, and 5 parts of sulphuric acid until the black colour of the manganese has disappeared, and then the chloride is distilled off.

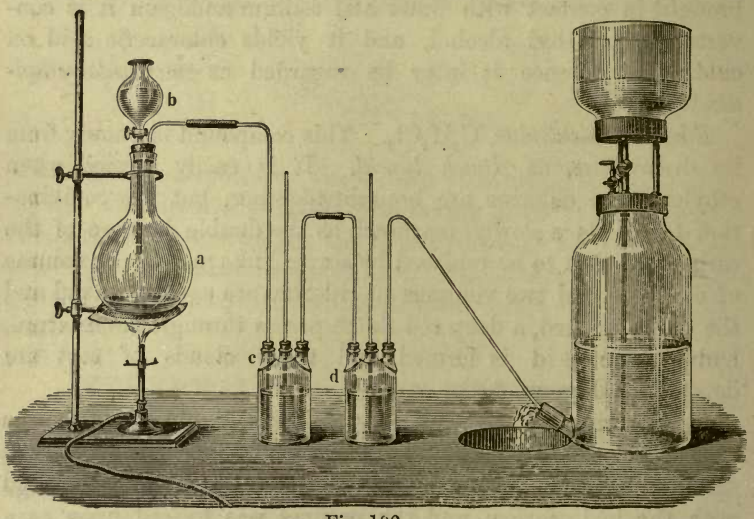



Fig. 100.

Coal-gas may also be employed as a source of ethylene, but in this case propylene chloride and higher homologues are formed, along with other chlorinated products. Nearly pure ethylene dichloride may, however, be separated from this mixture by fractional distillation.[1]

The latter compound is also formed by the action of ethylene on antimony pentachloride, chromium oxychloride, and cupric chloride. If the latter salt be fused in an atmosphere of the gas, large bubbles are evolved, which ignite and burn with a red flame with formation of hydrochloric acid and deposition of soot.[2]

[1] *Ann. Chem. Pharm.* xciv. 245. [2] Wöhler, *Pogg. Ann.* xiii. 297.

Ethylene dichloride is also obtained by treating glycol with pentachloride of phosphorus (Wurtz), or by heating ethylene alcohol with an excess of fuming hydrochloric acid to 100°.[1] It is also found in large quantity, together with ethyl chloride and other bodies, in the by-products in the manufacture of chloral (see part i. p. 539). According to Krämer,[2] it is here produced, together with its isomeride ethidene chloride, by the action of chlorine on ethyl chloride; whilst according to Städel[3] this latter compound only yields ethidene chloride as a further substitution-product.

Ethylene dichloride is a thin oily liquid, insoluble in water and possessing a pleasant smell and sweet taste. It boils at 83°·5, and at 0° has a specific gravity of 1·28082,[4] whilst that of its vapour is 3·44 (Gay-Lussac).

## CHLORINE SUBSTITUTION-PRODUCTS OF ETHYLENE.

A description of these compounds may here follow, as ethylene dichloride serves as their point of departure.

*Monochlorethylene* or *Vinyl Chloride*, $C_2H_3Cl$, was discovered by Liebig and afterwards investigated by Regnault.[5] In order to prepare it, ethylene dichloride is brought in contact with alcoholic potash and allowed to stand for some days until no further chloride of potassium separates out. The mixture is then warmed gently and the gas led through a vessel cooled with ice, and passing, for the purpose of purification, through sulphuric acid and caustic potash. Monochlorethylene is a gas having an ethereal smell, and condensing in a freezing mixture to a mobile liquid boiling between −18° and −15°. It is also formed by the action of alcoholic potash on ethidene dichloride, $CH_3.CHCl_2$. Exposed to sunlight it is converted into a viscous amorphous insoluble mass.

If the gas be passed into antimony pentachloride it is quickly absorbed, *monochlorethylene dichloride*, $CH_2Cl–CHCl_2$, being formed. This same body is also produced when ethylene

[1] Schorlemmer, *Journ. Chem. Soc.* 1881, i.
[2] *Ber. Deutsch. Chem. Ges.* iii. 259.
[3] *Ann. Chem. Pharm.* cxcv. 183.
[4] Thorpe, *Journ. Chem. Soc.* 1880, i. 182.
[5] *Ann. Chim. Phys.* lviii. 308.

dichloride is treated with chlorine in the sunlight. It is likewise found in the by-products of the chloral manufacture.[1] It is a liquid smelling like ethylene chloride, boiling at 115° and having a specific gravity at 0° of 1·4223.[2]

*Dichlorethylene*, $CH_2{=}CCl_2$, is produced by the action of alcoholic potash on the last-named compound (Regnault). It is a mobile liquid boiling at 37° (Krämer), and having a specific gravity at 15° of 1·250. Dichlorethylene passes very quickly into a white amorphous polymeric modification, insoluble in the ordinary solvents. It unites with chlorine to form *dichlorethylene dichloride*, $CH_2Cl{-}CCl_3$, a body which, however, has not been prepared pure in this way. It is formed, together with its isomeride acetylene tetrachloride, $CHCl_2{-}CHCl_2$ (a body which will be described further on), by the action of chlorine on ethylene dichloride and monochlorethylene dichloride, and is a liquid boiling at 127°·5.[3]

*Trichlorethylene*, $CHCl{=}CCl_2$, is obtained by acting with alcoholic potash on either of the isomeric chlorides, $C_2H_2Cl_4$, as well as by treating tetrachlorethylene or hexchlorethane with zinc and dilute sulphuric acid.[4] It is a liquid, boiling at 90°, and combines with chlorine to form *trichlorethylene dichloride*, $CHCl_2{-}CCl_3$, which is also formed by the continued action of chlorine on the foregoing bodies or on ethyl chloride. For this reason it is also termed *pentachlorethane*. It is readily prepared by the action of phosphorus pentachloride on chloral.[5] It is a liquid having a sweet burning taste and a pleasant honey-like smell, boiling at 159° and having at 0° a specific gravity of 1·7089.[6]

*Tetrachlorethylene*, $C_2Cl_4$. This compound, which was formerly called protochloride of carbon, was obtained by Faraday, in 1821, by passing the vapour of hexchlorethane, $C_2Cl_6$, through a red-hot tube.[7] Regnault prepared it from the latter compound by acting upon it with alcoholic solution of potassium hydrosulphide:[8]

$$C_2Cl_6 + 2KSH = C_2Cl_4 + 2KCl + SH_2 + S.$$

[1] Krämer, *Ber. Deutsch. Chem. Ges.* iii. 259.
[2] Pierre, *Ann. Chem. Pharm.* lxxx. 127.
[3] Städel, *Ann. Chem. Pharm.* cxcv. 187.
[4] Fischer, *Jahresb.* 1864, 481.
[5] Paterno, *Comptes Rendus*, lxviii. 450; *Ann. Chem. Pharm.* cli. 117.
[6] Thorpe, *Journ. Chem. Soc.* 1880, i. 192.
[7] *Phil. Trans.* 1821, 47.
[8] *Ann. Chem. Pharm.* xxx. 350; xxxiii. 324.

It is also formed from hexchlorethane by the action of reducing agents, such as zinc and dilute sulphuric acid or zinc filings in presence of alcohol.[1] The reduction in this way may readily go further, and, according to Bourgoin, a pure product is obtained by dissolving hexchlorethane in double its weight of aniline and heating this to 170°. The distillate, which still contains some of the higher chlorinated compound, is distilled with an equal weight of aniline at 130°—140°, and the distillate then freed from aniline by dilute sulphuric acid.[2]

It is a highly refracting mobile liquid, boiling at 121°, and at 0° having a specific gravity of 1·6595, whilst that of its vapour is 5·82 (Regnault).

It again combines with dry chlorine in the sunlight to form hexchlorethane, but when placed under a layer of water, trichloracetic acid is also formed. When tetrachlorethylene is heated with sulphur trioxide to 150°, trichloracetyl chloride is formed:

$$CCl_2{=}CCl_2 + SO_3 = CCl_3{-}COCl + SO_2.$$

*Hexchlorethane*, $C_2Cl_6$, was first prepared by Faraday by the continued treatment of ethylene chloride with chlorine. It is the final product of the action of this element on ethyl chloride and on all the foregoing substitution-products. It may be formed synthetically by passing a mixture of hydrogen and tetrachlormethane vapour through a red-hot tube:[3]

$$\begin{array}{ccccc} CCl_4 & & H & & CCl_3 \\ & + & | & = & | \\ CCl_4 & & H & & CCl_3 \end{array} + \begin{array}{c} HCl \\ \\ HCl. \end{array}$$

Hexchlorethane crystallizes in rhombic prisms and has a strong aromatic camphor-like smell. It is tolerably soluble in alcohol, still more so in ether, but scarcely dissolves in water. When heated, it sublimes at a temperature below its melting point, which lies at 185°—187°. In order to bring the liquid to the boiling point it must be heated under pressure. When the pressure is reduced to one atmosphere a sudden solidification takes place, from which it appears that the melting point of this compound lies somewhat higher than its boiling point.[4]

*Ethylene Bromhydrin*, $C_2H_4Br(OH)$, is obtained by saturating ethylene glycol with hydrobromic acid, and heating the solution to

[1] Geuther, *ib.* cvii. 212.
[2] Bourgoin, *Bull. Soc. Chim.* xxiii. 244.
[3] Stadeler, *Ann. Chem. Pharm.* Suppl. vii. 168.
[4] Hahn, *Ber. Deutsch. Chem. Ges.* xi. 1735.

100°. It is a thickish pleasantly smelling liquid which has a bitter taste. It boils at 147°, and has at 8° a specific gravity of 1·66, that of its vapour being 4·3025.[1]

474 *Ethylene Dibromide*, $C_2H_4Br_2$, was first prepared by Balard.[2] It is easily formed by passing ethylene into well-cooled bromine which is covered by a layer of water. In order not to be inconvenienced by the bromine vapours which are evolved, the arrangement suggested by Hofmann[3] is employed. A strong glass bottle of two to three liters capacity is filled with ethylene under water, and 120 grams of bromine together with the same quantity of water are poured in, and the cork quickly replaced by one carrying a glass tube which passes nearly to the bottom of the vessel, and being connected by a caoutchouc tube with a gas-holder containing ethylene. The gas is now allowed to pass in, the whole being shaken until no more absorption takes place. More bromine is then added, and the operation repeated until a sufficient quantity of the dibromide is obtained.

In order to prepare larger quantities, the method described by Erlenmeyer and Bunte, and shown in Fig. 101, may be used. The ethylene is prepared by the method already described, and, in order to obtain it as pure as possible, it is passed through an empty bottle (*a*) to condense any vapours of ether and alcohol which may be present; the bottle (*b*) containing sulphuric acid retains any of these products which are not condensed in (*a*), whilst (*c*) and (*d*) contain caustic soda.

The air is first driven out of this part of the apparatus, and the bottle (*e*) two-thirds filled with bromine and water, and connected on one side with the upright tube R, and on the other side with the bottle (*f*), which is filled to a height of five cm. with broken glass, and then with lumps of dry soda-lime. The air is now driven out so that the tube R is half filled with bromine, and the tube connected with the bottle (*d*), and ethylene is passed in until the colour of the bromine has disappeared. The crude product is purified by washing with caustic soda and water, then dried over calcium chloride, and rectified.

Ethylene bromide is a mobile pleasantly smelling liquid, having a sweet taste, boiling at 131°·5, and having a specific gravity at 0° of 2·2132 (Thorpe), whilst that of its vapour is 6·485 (Regnault). It solidifies in the cold to crystals which melt at 9°·5 (Regnault).

[1] Henry, *Ann. Chim. Phys.* [4], xxvii. 250. [2] *Ib.* [1], xxxii. 375.
[3] *Journ. Chem. Soc.* xiii. 67.

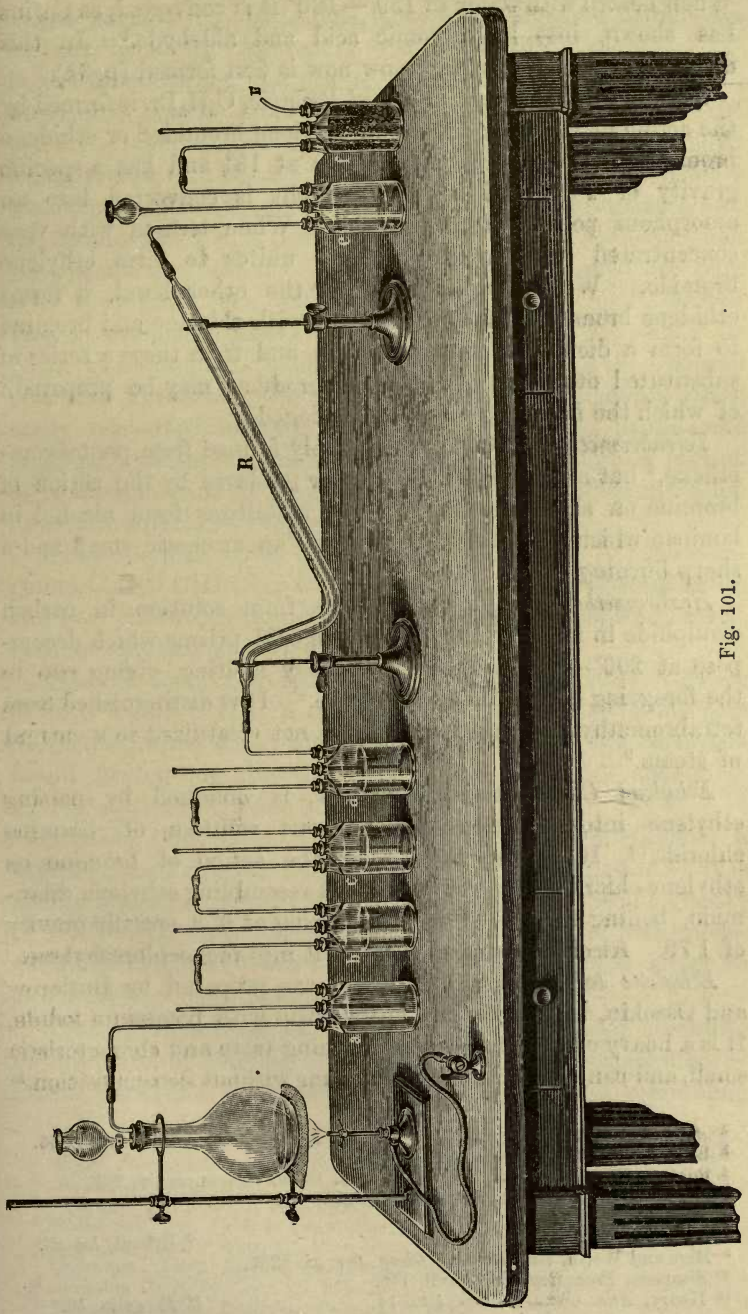



Fig. 101.

When heated with water to 150°—160° it is converted, as Carius has shown, into hydrobromic acid and aldehyde.[1] In this decomposition glycol as we know now is first formed (p. 34).

475 *Monobromethylene*, or *Vinyl Bromide*, $C_2H_3Br$, is formed by the action of alcoholic potash on ethylene bromide,[2] or ethidene bromide.[3] It is a liquid which boils at 18°, and has a specific gravity of 1·56; and in the sunlight is converted into an amorphous polymeric modification. When treated with very concentrated hydrobromic acid, it unites to form ethylene bromide. With a weak acid, on the other hand, it forms ethidene bromide.[4] It combines also with chlorine and bromine to form a dichloride and dibromide, and from these a series of substituted ethylenes and additive-products may be prepared,[5] of which the following may be mentioned.

*Tetrabromethylene*, $C_2Br_4$, is not only formed from pentabromethane,[6] but also together with other products by the action of bromine on alcohol or ether.[7] It crystallizes from alcohol in laminae which melt at 53°, and have an aromatic smell and a sharp burning taste.

*Hexbromethane*, $C_2Br_6$, crystallizes from solution in carbon disulphide in thick transparent tetragonal prisms which decompose at 200°—210° without previously melting, giving rise to the foregoing compound and bromine.[8] It is distinguished from tetrabromethylene, inasmuch as it is not volatilized in a current of steam.[9]

*Ethylene Chlorbromide*, $C_2H_4ClBr$, is obtained by passing ethylene into a well-cooled aqueous solution of bromine chloride.[10] It is also formed by the action of bromine on ethylene chloriodide,[11] and is a liquid resembling ethylene dibromide, boiling at 107°—108°, and having at 0° a specific gravity of 1·79. Alcoholic potash converts it into monochlorethylene.

*Ethylene Iodhydrin*, $C_2H_4I(OH)$, was prepared by Butlerow and Ossokin, by heating the chlorhydrin with potassium iodide. It is a heavy oily liquid having a burning taste and characteristic smell, and can be distilled in a vacuum without decomposition.[12]

[1] *Ann. Chem. Pharm.* cxxxi. 173. [2] Regnault, *Ann. Pharm.* xv. 63.
[3] Beilstein, *Bull. Soc. Chim.* 1861, 121.
[4] Reboul, *Comptes Rendus*, liv. 1229; *Ann. Chem. Pharm.* cxxiv. 267.
[5] See Denzel, *Ann. Chem. Pharm.* cxcv. 295.
[6] Lennox, *Proc. Roy. Soc.* xi. 257.
[7] Löwig, *Pogg. Ann.* xvi. 377. [8] Reboul, *loc. cit.*
[9] Merz and Weith, *Ber. Deutsch. Chem. Ges.* xi. 2239.
[10] Simpson, *Proc. Roy. Soc.* xxvii. 118.
[11] Henry, *Ann. Chem. Pharm.* clvi. 14. [12] *Ib.* cxliv. 42.

476 *Ethylene Di-iodide*, $C_2H_4I_2$, was first prepared by Faraday in 1821, by acting on ethylene with iodine in the sunlight.[1] It is also formed when the gas is passed into iodine warmed to 50°—60°.[2] It is, however, best prepared according to the process of Semenoff, by passing ethylene into finely-powdered iodine mixed with alcohol so as to form a thin paste. When a considerable quantity of the compound has been separated out, the iodine solution is poured off, mixed again with iodine, and the operation repeated. The crystals thus obtained are pure after they have been washed with cold alcohol.[3] It crystallizes in colourless tables or prisms melting at 81°—82°.[4] It possesses an aromatic smell, and the vapour attacks the eyes and produces headache. It is a very unstable compound, being easily converted in the presence of light into iodine and ethylene. When heated it also decomposes, though a portion of it sublimes, and it may be sublimed without decomposition in an atmosphere of ethylene.

When ethylene iodide is heated with alcohol to 70°, the compound $C_2H_5O.CHI.CH_3$ is formed. This is *moniodethyl oxide*, and is a yellow oily liquid having a sharp overpowering smell. Sodium ethylate converts it into acetal.[5]

Alcoholic potash converts ethylene di-iodide into *moniodethylene* or *vinyl iodide*, $C_2H_3I$,[6] a decomposition which may easily pass on further, when much acetylene is evolved.[7] It is a colourless liquid having an alliaceous smell, boiling at 56° and at 0° having a specific gravity of 2·08.

*Ethylene Chloriodide*, $C_2H_4ClI$, is formed when ethylene is passed into an aqueous solution of iodine monochloride.[8] It is an oily liquid boiling at 140°, and at 10° having a specific gravity of 2·1644 (Thorpe). Alcoholic potash converts it into monochlorethylene, and when heated with finely divided silver to 160° ethylene and ethylene-dichloride are formed.[9]

*Ethylene Bromiodide*, $C_2H_4BrI$. This body is formed, according to Simpson, by passing ethylene into an aqueous solution of iodine bromide. It is deposited in white needles resembling

[1] *Quart. Journ. Science*, xiii. 429. [2] Regnault, *Ann. Pharm.* xv. 67.
[3] *Zeitsch. Chem.* 1864, 673.
[4] Aronstein and Kramps, *Ber. Deutsch. Chem Ges.* xiii. 489.
[5] Baumstark, *Ber. Deutsch. Chem. Ges.* vii. 1172.
[6] Regnault, *Ann. Pharm.* xv. 63.
[7] Gustavson, *Journ. Russ. Chem. Ges.* vi. 164.
[8] Simpson, *Proc. Roy. Soc.* xii. 278.
[9] Friedel and Silva, *Bull. Soc. Chim.* xvii. 242.

ethylene iodide, melts at 28°, and boils between 162° and 167°.[1]

477 *Sulphates of Ethylene.* When ethylene alcohol is heated with concentrated sulphuric acid to 150°, it forms *ethylene-hydroxy-sulphuric acid,* $C_2H_4(OH)SO_4H$, a body which is not known in the pure state. The barium salt is easily soluble, it forms a white solid mass which decomposes readily in aqueous solution with formation of glycol, sulphuric acid, and barium sulphate.[2]

*Ethylenesulphuric Acid,* $C_2H_4(SO_4H)_2$, is formed when glycol is allowed to fall drop by drop into chlorsulphonic acid which is cooled by ice :

$$2SO_2\begin{cases}Cl\\OH\end{cases} + C_2H_4\begin{cases}OH\\OH\end{cases} = C_2H_4\begin{cases}OSO_2.OH\\OSO_2.OH\end{cases} + 2HCl.$$

It is a thick liquid, which decomposes only at 160°; on heating with water is resolved into sulphuric acid and glycol. Its barium salt, $C_2H_4(SO_4)_2Ba + 2H_2O$, crystallizes in slender interwoven needles.[3]

*Ethylene Nitrite,* $C_2H_4(NO_2)_2$. This compound was first obtained by Semenoff by passing ethylene into liquid nitrogen tetroxide. An oily, very poisonous body is formed at the same time, but this has not been further investigated. The nitrite may be obtained in the purer state by passing ethylene into pure ether, and at the same time allowing nitrogen tetroxide to drop in. Ethylene nitrite crystallizes in tables or prisms which fuse at 37°·5, and sublime at a higher temperature with partial decomposition.[4] It has not yet been ascertained whether this compound is a nitrous ether or dinitro-ethylene, though the former of these views is the more probable, as amyl nitrite prepared in a similar way is doubtless a nitrous ether.

When tetrachlorethylene is heated with nitrogen tetroxide to 110°—120°, dinitro-tetrachlorethylene, $C_2Cl_4(NO_2)_2$, is formed, a body crystallizing from alcohol in feathery needles. It smells like chlorpicrin, and is easily decomposed on heating, but sublimes in a current of aqueous vapour.[5]

*Ethylene Nitri-nitrate,* $C_2H_4\begin{cases}ONO\\ONO_2\end{cases}$, is formed when ethylene is passed into a well-cooled mixture of concentrated nitric and sulphuric acids. It is a colourless oily liquid having a

[1] Simpson, *Proc. Roy. Soc.* xxii. 51. [2] *Ib.* ix. 725.
[3] Claesson, *Journ. Prakt. Chem.* [2], xx. 2.
[4] *Zeitsch. Chem.* 1864, 673. [5] Kolbe, *Ber. Deutsch. Chem. Ges.* ii. 326.

spirituous and pungent smell, the vapour attacking the eyes and producing headache. On heating, decomposition takes place. Alkalis, as well as dilute hydriodic acid, convert it into ethylene alcohol, a reaction which shows that it is not a nitro-compound.[1]

*Ethylene Nitrate*, $C_2H_4(ONO_2)_2$, is produced when ethylene glycol is gradually added to a well-cooled mixture of concentrated nitric and sulphuric acids. It is a colourless oily liquid having an unpleasant sweet taste, and taking fire readily, burning quickly with a bright flame. It decomposes on percussion, is poisonous, and is converted into ethyl alcohol in presence of caustic potash.[2]

In a similar way *Ethylene Chlornitrate*, $C_2H_4Cl.NO_3$, is obtained from ethylene chlorhydrin, and this substance is also a heavy oily liquid (Henry).

478 *Borate of Ethylene.* By the action of boron trioxide on ethylene alcohol the monoborether is obtained:

$$B\begin{cases}Cl\\Cl\\Cl\end{cases} + 3C_2H_4(OH)_2 = B\begin{cases}O.C_2H_4.OH\\O.C_2H_4.OH\\O.C_2H_4.OH\end{cases} + 3HCl.$$

It separates out from its solution in chloroform in yellowish-white microscopic laminæ which are decomposed by water into boric acid and glycol. It is not combustible, but colours the luminous gas flame of a bright green.[3]

*Ethylene Thiocyanate*, $C_2H_4(SCN)_2$, is formed by heating ethylene bromide with alcoholic solution of potassium thiocyanate. It is slightly soluble in cold water, and more easily soluble in hot water and in alcohol. It crystallizes in needles or rhombic tables, melting at 90°, and having a sharp taste. Its smell is peculiar. When boiled with water it volatilizes, its vapour attacking the eyes.[4]

*Ethylene Selenocyanate*, $C_2H_4(SeCN)_2$, is obtained in a similar way to the foregoing, from potassium selenocyanate. It crystallizes from boiling water or alcohol in fine white needles, which melt with decomposition at 128°.[5]

*Ethylene Diformate*, $C_2H_4(CHO_2)_2$ is formed by boiling glycol

[1] Kekulé, *Ber. Deutsch. Chem. Ges* ii. 329.

[2] L. Henry, *Ber. Deutsch. Chem. Ges.* iii. 529; Champion, *Compt. Rend.* lxxiii. 571.

[3] Councler, *Ber. Deutsch. Chem. Ges.* xi. 1106.

[4] Buff, *Ann. Chem. Pharm.* xcvi. 362; c. 228; Sonnenschein and Meyer, *Journ. Prakt. Chem.* lxv. 257.

[5] Proskauer, *Ber. Deutsch. Chem. Ges.* vii. 1280.

with 3 to 4 parts of 75 to 80 per cent. formic acid in connection with an inverted condenser. The product is then distilled, and a liquid obtained which boils between 170°—180°, and this also contains monoformate. In order to remove this latter compound it is again heated with formic acid, and the pure ether is obtained by rectification of the product. It is a mobile liquid having a peculiar smell and boiling at 174°.[1]

479 *Ethylene Monacetate*, or *Ethylene Monacetin*, $C_2H_4\left\{\begin{matrix}OH\\OC_2H_3O.\end{matrix}\right.$ The formation of this compound has already been described under glycol. It is obtained by fractional distillation as an oily liquid having a neutral reaction, a faint smell resembling acetic acid, and boiling at 182°. It is heavier than water, and miscible with this liquid. The ether is also formed when glycol is heated to 200° with the necessary quantity of acetic acid.[2] If acetic anhydride be employed in place of acetic acid, the reaction takes place at 170°.[3]

*Ethylene Diacetate*, or *Ethylene Diacetin*, $C_2H_4(OC_2H_3O)_2$, is best obtained, according to Wurtz, by mixing 5 parts of ethylene bromide and 9 parts of silver acetate with acetic acid until they form a thin paste, and heating this for some days to 100°. It is then washed out with ether, the latter distilled off, and the residue fractionated. It is also obtained by heating glycol with excess of acetic acid to 200° (Laurenço). Ethylene diacetate is a colourless liquid, having a specific gravity at 0° of 1·128, and boiling at 186°—187°. On heating it has a faint smell of acetic acid, and it dissolves at 22° in 7 parts of water, separating out again on addition of calcium chloride.

*Ethylene Chloracetin*, or *Ethylene Acetochloride*, $C_2H_4\left\{\begin{matrix}Cl\\O.C_2H_3O,\end{matrix}\right.$ is obtained by heating a mixture of glycol and acetic acid saturated with hydrochloric acid, or better by passing hydrochloric acid gas into ethylene monacetin heated to 100° (Simpson). It is also formed by the action of acetyl chloride on glycol (Laurenço). It is a liquid boiling at 145°, and having at 0° a specific gravity of 1·1783.

*Ethylene Iodacetin*, $C_2H_4\left\{\begin{matrix}I\\O.C_2H_3O,\end{matrix}\right.$ is formed in a similar way to the foregoing compound by the action of hydriodic acid

[1] Henninger, *Bull. Soc. Chim.* [2], xxi. 242.
[2] Laurenço, *Ann. Chim. Phys.* [3], lxvii. 267.
[3] Simpson, *Proc. Roy. Soc.* x. 114.

on the cold monacetin. It is an oily, sweetish liquid, which on cooling crystallizes in tables (Simpson).

Besides these ethers the following may be mentioned. They have been prepared by Laurenço, Simpson, and Wurtz:

| | | B.P. |
|---|---|---|
| Ethylene monobutyrate, | $C_2H_4\left\{\begin{matrix}OH\\O.C_4H_7O\end{matrix}\right.$ | about 220°. |
| Ethylene acetobutyrate, | $C_2H_4\left\{\begin{matrix}O.C_2H_3O\\O.C_4H_7O\end{matrix}\right.$ | 208 to 215°. |
| Ethylene dibutyrate, | $C_2H_4\left\{\begin{matrix}O.C_4H_7O\\O.C_4H_7O\end{matrix}\right.$ | 239 to 241°. |
| Ethylene monovalerate, | $C_2H_4\left\{\begin{matrix}OH\\O.C_5H_9O\end{matrix}\right.$ | about 240°. |
| Ethylene acetovalerate, | $C_2H_4\left\{\begin{matrix}O.C_2H_3O\\O.C_5H_9O\end{matrix}\right.$ | ,, 230°. |
| Ethylene divalerate, | $C_2H_4\left\{\begin{matrix}O.C_5H_9O\\O.C_5H_9O\end{matrix}\right.$ | ,, 255°. |

## SULPHUR COMPOUNDS OF ETHYLENE.

480 *Ethylene Hydroxysulphide*, $C_2H_4\left\{\begin{matrix}OH\\SH\end{matrix}\right.$, was obtained by Carius by acting on potassium hydrosulphide with ethylene chlorhydrin. It is a colourless liquid heavier than water, having a faint smell of mercaptan. Its alcoholic solution gives precipitates with many metallic salts.[1]

*Ethylene Dihydrosulphide*, or *Ethylene Mercaptan*, $C_2H_4(SH)_2$. The existence of this compound was observed so long ago as 1840 by Löwig and Weidmann, but it was first prepared in the pure state in 1862 by Werner. It is easily formed by the action of ethylene bromide on potassium hydrosulphide in alcoholic solution. It is a colourless highly refracting liquid, boiling at 146°, and having a specific gravity of 1·123 at 23°·5. It dissolves easily in ammonia and other alkalis, and forms insoluble mercaptides with the heavy metals.[2]

*Ethylene Sulphide*, $C_2H_4S$, is obtained by the action of an alcoholic solution of potassium sulphide on ethylene bromide,

[1] Carius, *Ann. Chem. Pharm.* cxxiv. 257.
[2] *Zeitsch. Chem.* 1862, 584.

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and was first prepared by Löwig and Weidmann as a white amorphous powder, and termed by them *sulphetherin*.[1]

The body was then examined almost simultaneously by Crafts,[2] Werner,[3] and Husemann,[4] and obtained by the action of an alcoholic solution of potassium sulphide on ethylene bromide. According to Crafts the product contains bromine, but if it be submitted to a careful dry distillation, a white crystalline body of the above composition is obtained, and this is purified by heating the first product for some days in contact with ether, alcohol, or carbon disulphide to 150°—160°. Husemann found, moreover, that this compound may be obtained by heating mercury ethylene mercaptide with ethylene bromide:

$$C_2H_4\langle{}^{S}_{S}\rangle Hg + C_2H_4Br_2 = C_2H_4\langle{}^{S}_{S}\rangle C_2H_4 + HgBr_2.$$

Hence this compound is *diethylene disulphide*, and its constitution is analogous to that of diethylene dioxide. Its vapour density was also found to correspond to this, being 4·28.

Diethylene disulphide crystallizes from hot alcohol in white glistening needles, and from ether in hard, glassy, monoclinic prisms. It has a powerful smell and pungent taste, sublimes at 111° and boils at about 200°.

It unites directly with the elements of the chlorine group. The compound with iodine is comparatively stable, crystallizing in monoclinic tables, having the formula $(C_2H_4)_2S_2I_4$, or perhaps $C_2H_4SI_2$. The crystals appear red by transmitted light, but have a metallic or an iron-black lustre by reflected light.

Concentrated nitric acid converts the disulphide into $(C_2H_4)_2S_2O_2$, a body crystallizing from hot water in white needles. Heated under pressure, $(C_2H_4)_2S_2O_4$, or $C_2H_4SO_2$, is produced, a body which forms crystals insoluble in water.

*Ethylene Thiocarbonate*, $C_2H_4.CS_3$, is formed by the action of sodium thiocarbonate on ethylene bromide. It crystallizes from ether-alcohol in fine golden-yellow prisms, melting at 36°·5. It is oxidized by dilute sulphuric acid to *ethylene oxythiocarbonate*, $C_2H_4.COS_2$, which crystallizes from alcohol in thin needles, melting at 31°.

481 *Ethylene Thiochlorides.* These bodies, discovered by

[1] *Pogg. Ann.* xlix. 123.
[2] *Ann. Chem. Pharm.* cxxiv. 110; cxxviii. 220.
[3] *Zeitsch. Chem.* 1862, 584.
[4] *Ann. Chem. Pharm.* cxxvi. 269.

Guthrie,[1] are formed by the direct union of ethylene with the chlorides of sulphur.

*Ethylene Thiodichloride*, $C_2H_4SCl_2$, is formed by passing ethylene into well-cooled sulphur dichloride, which must be afterwards heated to 100°. It is a liquid having a taste and smell resembling mustard-oil. It produces blisters when brought on the skin, and at the ordinary temperature gives off a small amount of vapour which attacks the mucous membranes. It decomposes easily on heating.

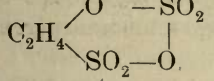
*Ethylene Dithiodichloride*, $(C_2H_4)_2S_2Cl_2$, is formed by heating ethylene with sulphur monochloride to 100°. It is a light-yellow liquid having a sweet pungent odour and taste, the vapours of which attack the eyes powerfully.

*Chlorethylene Dithiodichloride*, $(C_2H_3Cl)_2S_2Cl_2$, is formed by the action of ethylene on boiling sulphur monochloride. It is a light-yellow liquid having a sweet biting taste and a pleasant odour resembling that of lemons and peppermint.

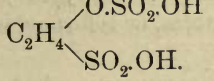
## Sulpho-acids of Ethylene.

**482** Regnault, in 1837, was the first to point out that ethylene unites with the vapour of sulphur trioxide, forming the crystalline compound $C_2H_4S_2O_6$, to which he gave the name of sulphacetylic acid.[2] The same body was obtained by Magnus by acting with alcohol on sulphur trioxide. He termed it *carbyl sulphate*, and found that, in contact with water, it gives rise to a dibasic acid, to which he gave the name of *ethionic acid*, $C_2H_4S_2O_7H_2$, but that when boiled with water it is converted into monobasic *isethionic acid*, $C_2H_5SO_4H$, and sulphuric acid.[3] Later investigations have proved that the last-named acid is a sulphonic acid, and that these compounds have the following constitution:

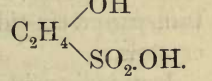
Carbyl Sulphate.



Ethionic Acid.



Isethionic Acid.



*Isethionic Acid* or *Hydroxyethylene Sulphonic Acid.* Before the discovery of carbyl sulphate, this substance was prepared by

[1] *Journ. Chem. Soc.* xiii. 35 ; *ib.* 129 ; xiv. 128.
[2] *Ann. Chem. Pharm.* xxv. 32.
[3] *Pogg. Ann.* xlvii. 509.

Magnus from ethionic acid, a compound which he had obtained by treating alcohol or ether with sulphur trioxide and dissolving the product in water. Magnus thought at first that the two acids were isomerides and, as Sertürner had suggested for sulphovinic acid (ethyl sulphuric acid), the name of oenothionic acid, Magnus adopted the above names for his acids, as both might be considered to be compounds of ether and anhydrous sulphuric acid.[1]

Isethionic acid is also formed in an analogous way to the other sulphonic acids by oxidizing ethylene hydroxysulphide (p. 51) with nitric acid, and its potassium salt is formed when an aqueous solution of acid sodium sulphite is heated with ethylene oxide to 100°.[2] It is also found, in an analogous way, from normal sodium sulphite and ethylene chlorhydrin at a temperature of 170°—180°.[3]

In order to prepare it, the vapour of sulphur trioxide is passed into well-cooled absolute alcohol or ether, the product diluted with four times its volume of water and boiled for some hours, the evaporated water being from time to time replaced. It is then saturated with barium carbonate and filtered. The liquid is concentrated by evaporation until crystals of barium methylene disulphonate (Part I. p. 264), separate out, whilst the rest of the salt is thrown down on addition of alcohol. The filtrate is then concentrated to the consistency of a thin syrup, and, on standing, barium isethionate separates out, and this is decomposed by dilute sulphuric acid. On evaporating the solution, isethionic acid remains as a syrup but crystallizes to deliquescent needles having a strongly acid taste, when allowed to evaporate over concentrated sulphuric acid.

The salts of isethionic acid are readily soluble and crystalline. *Potassium Isethionate*, $C_2H_4(OH)SO_3K$, crystallizes in glistening laminae or rhombic prisms. *Ammonium Isethionate*, $C_2H_4(OH)SO_3NH_4$, is deposited in transparent prisms or pyramids. *Barium Isethionate*, $[C_2H_4(OH)SO_3]_2Ba$, crystallizes in transparent six-sided tables, or is formed in large semi-transparent crystals.

Isethionic acid also acts as an alcohol, and hence it exhibits elations similar to the hydroxy-acids of the lactic series. Thus, on oxidation, it is converted into sulphonacetic acid,

[1] *Pogg. Ann.* xxvii. 378.
[2] Erlenmeyer and Darmstädter, *Zeitsch. Chem.* 1868, 342.
[3] Collmann, *Ann. Chem. Pharm.* cxlviii. 101.

$CH_2(SO_3H)CO_2H$,[1] a body which will be described under the glycolyl compounds.

*Isethionyl Dichloride*, $C_2H_4Cl(SO_2Cl)$, is obtained by the action of phosphorus pentachloride on potassium isethionate. It is a heavy colourless oil, smelling like oil of mustard, and boiling at about 200°.

*Chlorisethionic Acid*, $C_2H_4Cl(SO_3H)$. The chloride is only slowly attacked by water at the ordinary temperature, and in order to prepare this acid the mixture must be heated for some days in closed tubes. Chlorisethionic acid crystallizes in deliquescent needles and forms salts which crystallize well. On boiling with water, especially in presence of an alkali, isethionic acid is again formed.[2]

## Amidisethionic Acid, or Taurine, $C_2H_4(NH_2)SO_3H$.

483 This body was discovered in 1824 by Leopold Gmelin[3] in ox-bile, and afterwards investigated more completely by Demarçay,[4] and by Pelouze and Dumas.[5] These chemists, however, overlooked the fact that taurine contained sulphur, and gave to it the formula $C_2H_7NO_5$. Its correct composition was, however, ascertained by Redtenbacher.[6]

Taurine occurs in bile in the free state, but chiefly in combination with cholic acid as taurocholic acid. It is also found in the kidneys, lungs, muscles, &c.

In order to prepare it from ox-bile an excess of hydrochloric acid is added, the whole filtered and evaporated until a treacly resinous mass separates out. The watery liquid is then poured off and evaporated, when common salt separates out, formed from the sodium salts of the bile acids. The solution which is poured off, is mixed with strong alcohol, and set aside until the whole of the taurine crystallizes out. Alcohol is then added and the whole purified by recrystallization.

Kolbe first obtained taurine artifically by heating ammonium chlorisethionate with an excess of aqueous ammonia to 140°.[7]

Taurine is tolerably soluble in cold, and very soluble in hot water, crystallizing in large transparent monoclinic prisms.

[1] F. Carl, *Ber. Deutsch Chem. Ges.* xiv. 63.
[2] Kolbe, *Ann. Chem. Pharm.* cxii. 241; cxxii. 33.
[3] Tiedemann and Gmelin, *Die Verdauung*, i. 43, 690.
[4] *Ann. Pharm.* xxvii. 286. [5] *Ib.* xxvii. 292.
[6] *Ib.* lvii. 170; lxv. 37.
[7] *Ann. Chem. Pharm.* cxxii. 33.

The crystals grate between the teeth, and have a cooling but not otherwise characteristic taste. Its aqueous solution has a scarcely preceptible acid reaction, and, from this solution, alcohol precipitates it in the form of small crystals, which under the microscope are seen to possess the characteristic prismatic form. It does not combine with acids, nor does it form salts of definite composition with bases. That it acts, however, as a weak acid is seen from the fact that it is not precipitated from its solution in alkalis by alcohol, but that it is thrown down when carbon dioxide is passed through the solution.

Like other amido-acids (Part I. p. 460) taurine must be considered as an ammonium salt, having the following composition :

$$\begin{array}{l} CH_2—NH_3 \\ | \quad | \\ CH_2.SO_2\,O. \end{array}$$

If nitrogen trioxide be passed into its solution in dilute nitric acid it is converted into isethionic acid.[1]

*Tauro-carbamic Acid*, $C_2H_4(NH.CO.NH_2)SO_3H$, is found in the urine when taurine is administered. It crystallizes in glistening quadratic laminæ, easily soluble in water. The potassium salt of this acid may be artificially prepared by evaporating mixed solutions of taurine and potassium cyanate. If the acid be heated with baryta solution to 130°—140° it decomposes into taurine, ammonia, and carbon dioxide.[2]

484 *Carbyl Sulphate* and *Ethionic Acid.* From the foregoing constitutional formula it is clear that ethionic acid is the sulphate of isethionic acid and carbyl sulphate the corresponding anhydride. To prepare this latter compound, sulphur trioxide is brought into a vessel well cooled with ice, and then a tube filled with absolute alcohol lowered into the flask and the whole tightly closed. When the sulphur trioxide has been absorbed, the tube is brought into another vessel containing trioxide, and the operation repeated until a sufficient quantity of the crystals have separated out, the fuming sulphuric acid which is produced at the same time being poured off. The crystals are brought on to a porous plate contained in a vacuum over sulphuric acid, and allowed to stand until they no longer fume. Carbyl sulphate forms a radiated mass of crystals, which melt at 80°; the fused mass crystallizing on cooling. It absorbs

[1] Gibbs, *Sillim. Am. Journ.* [2], xxv. 30.
[2] Saikowsky, *Ber. Deutsch. Chem. Ges.* vi. 744 and 1191.

moisture with great avidity, being converted into ethionic acid, which is only known in aqueous solution. Its salts usually crystallize well, but they also are very unstable.

*Di-isethionic Acid*, $O\begin{cases} C_2H_4SO_3H \\ C_2H_4SO_3H \end{cases}$. The salts of this acid are formed by gently heating the isethionates. The acid prepared from the barium salt has only been obtained as yet in the form of a thick syrup.

*Ammonium Di-isethionate*, $(C_2H_4SO_3NH_4)_2O$. By heating ammonium isethionate, Strecker obtained a body which he believed to be taurine.[1] Seyberth showed that this is not the case, and he considered this compound to be the amide of isethionic acid.[2] Its exact composition was, however, first determined by F. Carl. In order to prepare ammonium di-isethionate, ammonium isethionate is heated for some hours to 210°—220°, and the residue crystallized from boiling alcohol. It forms pearly glistening laminæ which melt at 196°—198°. When boiled with baryta water, the corresponding barium salt, $C_4H_8S_2O_7Ba + H_2O$, crystallizes out in thin six-sided tables. It is also formed when barium isethionate is heated for some time to 200°.

485 *Ethylene Disulphonic Acid*, $C_2H_4(SO_3H)_2$, was first prepared by Hofmann and Buckton[4] by heating propionamide or propionitril with fuming sulphuric acid, and termed by them disulphetholic acid:

$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CN \end{matrix} + 3SO_2(OH)_2 = \begin{matrix} CH_2.SO_2.OH \\ | \\ CH_2.SO_2.OH \end{matrix} + SO_2\begin{cases} ONH_4 \\ OH \end{cases} + CO_2.$$

Almost simultaneously, Buff[5] obtained it by oxidizing ethylene thiocyanate with nitric acid. It may also be obtained in the same way from ethylene dihydrosulphide and ethylene thio-carbonate. It is likewise easily formed by acting on acetic anhydride with concentrated sulphuric acid.[6] The free acid is a very deliquescent crystalline mass which yields easily soluble

[1] *Ann. Chem. Pharm.* xci. 97.
[2] *Ber. Deutsch. Chem. Ges.* vii. 391.
[3] *Ib.* xii. 1604; xiv. 65.
[4] *Proc. Roy. Soc.* viii. 158.
[5] *Ann. Chem. Pharm.* c. 232.
[6] Franchimont, *Compt. Rend.* xcii. 1054.

salts which usually crystallize well. These have been completely studied by Husemann.[1]

*Hydroxy-ethylene Disulphonic Acid*, $C_2H_3(OH)(SO_3H)_2$, is formed by heating potassium isethionate with fuming sulphuric acid. It forms a thick strongly acid syrup. Its salts are very stable and crystallize well.[2]

## NITROGEN BASES OF ETHYLENE.

**486** The action of ammonia on ethylene bromide was first investigated by Cloëz, who obtained three different bases, termed by him, Formyliac, $N(CH)H_2$; Acetyliac, $N(C_2H_3)H_2$; and Propyliac, $N(C_3H_5)H_2$.[3] At the same time Natanson examined this reaction and obtained similar bodies, but did not discover their chemical nature.[4] A clear light was, however, thrown upon this subject by the investigation of Hofmann,[5] who showed that the action of ethylene bromide upon ammonia is similar to that of the haloid ethers of the monatomic alcohol radicals, with this difference, that one molecule of ethylene bromide acts upon two molecules of ammonia, and that the bases thus formed are then further attacked by the ethylene bromide, as shown by the following reaction, in which graphic formulæ are used in place of Hofmann's typical formulæ:

Ethylene-diamine.

$$C_2H_4Br_2 + 2NH_3 = C_2H_4\begin{matrix}NH_2\\NH_2\end{matrix} + 2HBr.$$

Diethylene-diamine.

$$C_2H_4Br_2 + C_2H_4\begin{matrix}NH_2\\NH_2\end{matrix} = C_2H_4\begin{matrix}NH\\NH\end{matrix}C_2H_4 + 2HBr.$$

Triethylene-triamine.

$$C_2H_4Br_2 + C_2H_4\begin{matrix}NH\\NH\end{matrix}C_2H_4 = C_2H_4\begin{matrix}N\\N\end{matrix}C_2H_4\begin{matrix}N\\N\end{matrix}C_2H_4 + 2HBr.$$

The last compound unites with ethylene bromide to form tetraethylammonium dibromide, $N_2(C_2H_4)_4Br_2$.

[1] *Ann. Chem. Pharm.* cxxvi. 269. [2] Meves, *Ann. Chem. Pharm.* cxliii. 196.
[3] *Jahresb.* 1853, 468; *ib.* 1858, 344; *Comptes Rendus*, xlvi. 344.
[4] *Ann. Chem. Pharm.* xcii. 48; xcviii. 291.
[5] *Compt. Rend.* xlvi. 255; xlix. 781; *Proc. Roy. Soc.* x. 224.

At the same time other reactions take place in which polyethylamines corresponding to the polyethylene alcohols are formed:

Diethylene-triamine.

$$2C_2H_4Br_2 + 3NH_3 = \begin{matrix} C_2H_4.NH_2 \\ NH \\ C_2H_4.NH_2 \end{matrix} + 4HBr.$$

Triethylene-triamine.

$$C_2H_4Br_2 + \begin{matrix} C_2H_4.NH_2 \\ NH \\ C_2H_4.NH_2 \end{matrix} = \begin{matrix} C_2H_4.NH \\ NH \\ C_2H_4.NH \end{matrix} \begin{matrix} \\ \\ \end{matrix} C_2H_4 + 2HBr.$$

Triethylene-tetramine.

$$3C_2H_4Br_2 + 4NH_3 = \begin{matrix} C_2H_4.NH_2 \\ NH \\ C_2H_4 \\ NH \\ C_2H_4.NH_2 \end{matrix} + 6HBr.$$

&c.

In the case of diamines containing the groups $NH_2$ or NH the hydrogen in these groups may be replaced wholly or partially by alcohol radicals, by heating the diamines with the haloid ethers. Similar compounds are also formed when ethylene bromide is heated with the primary or secondary amines.

The tertiary amines, on the other hand, exhibit a different behaviour towards ethylene bromide. Apparently an addition-product of the two bodies is formed, but the substance produced is the monobromide of an ammonium containing the group $C_2H_4Br$, as for example, *trimethyl-bromethyl-ammonium bromide*, $N(CH_3)_3(C_2H_4Br)Br$. Silver salts precipitate only one half the bromine from this substance, whilst ammonia withdraws hydrobromic acid, *trimethyl-vinyl-ammonium bromide*, $N(CH_3)_3(C_2H_3)Br$, being formed. If moist silver oxide be used instead of ammonia, both bromine atoms are removed, and the hydroxide of the vinyl base, $N(CH_3)_3(C_2H_3)OH$, is produced.

From the foregoing, it is seen that the number of compounds of this group is numerous. As, however, these bodies resemble the compound ammonias and ammonium compounds in their

chemical relations, it will here be sufficient to describe the more important of them.

487 *Ethylene Diamine*, $C_2H_4(NH_2)_2$, is formed together with other of the above-named diamines when ethylene bromine acts for some time on alcoholic ammonia at 100°. The cooled liquid is then poured off from the ammonium bromide which separates out, evaporated to dryness, and the residue distilled with caustic potash. The distillate is dried over solid caustic potash, and then fractionated and the bases thus separated.

For the preparation of large quantities of ethylene diamine the by-product obtained in the manufacture of chloral, and boiling between 70° and 100°, can be utilized.[1] This is a mixture of ethylene chloride, ethidene chloride, and higher substitution-products, of which the two first-named are attacked by alcoholic ammonia at 100°—120°. As soon as the reaction is complete, the liquid is separated from the sal-ammoniac and the unaltered chlorine compounds distilled off. From the residue the hydrochloride of the base having the composition $C_2H_4(NH_3Cl)_2$ separates out in needles, and this is obtained in the form of silver-white needles after frequent recrystallization and washing with alcohol, in which it is insoluble. The brown mother-liquor is distilled with caustic potash, and the first distillate treated with hydrochloric acid, when another yield of the hydrochlorate is obtained. The later fractions contain the higher diamines, triamines, &c.

The compound obtained by distillation with caustic potash from the salts is not the anhydrous base but the hydrate $C_2H_4(NH_2)_2 + H_2O$, and from this the water cannot be withdrawn even by barium oxide, and it boils at almost the same temperature as the anhydrous base. Although the water is so intimately combined, the compound does not exist in the gaseous form. Cloëz found the specific gravity of the vapour to be 1·427, and hence he concluded that formyliac which he believed to be contained in the salts had the formula $N(CH)H_2$.

Anhydrous ethylene diamine can only be obtained by repeated distillation of the hydrate over sodium. It is a thick liquid having a faint ammoniacal smell, and a burning taste. It is strongly alkaline and easily soluble in water. It boils at 117° and has a vapour density of 2·07.

*Ethylene Diethyl Diamine*, $C_2H_4\begin{cases}NH(C_2H_5)\\NH(C_2H_5)\end{cases}$, is formed not

[1] *Ber. Deutsch. Chem. Ges.* iv. 666.

only by the action of ethylamine on ethylene bromide, but also by that of ethyl iodide on ethylene diamine. If the product be distilled with water and silver oxide, and the distillate allowed to evaporate in a vacuum, the hydrate $N_2C_2H_4(C_2H_5)_2H_2 + H_2O$ is obtained. It is a solid mass resembling stearic acid, having an ammoniacal smell, and losing water in contact with caustic baryta. The anhydrous base is a colourless oily liquid.[1]

*Diethylene Diamine*, $N_2(C_2H_4)_2H_2$, is a liquid boiling at 170° which unites with water to form the crystalline hydrate. By the action of ethyl iodide, the hydriodide of *diethylene diethyl diamine*, $N_2(C_2H_4)_2(C_2H_5)_2$, is formed. The free base boils at 185°.

*Triethylene Diamine*, $N_2(C_2H_4)_3$, boils at about 210°, and is easily soluble.

*Diethylene Triamine*, $N_3(C_2H_4)_2H_5$, is an oily liquid soluble in water and boiling about 208°. Treated with an excess of hydrochloric acid it yields the salt $N_3(C_2H_4)_2H_8Cl_3$, which crystallizes well and combines with platinum chloride to form the compound $[N_3(C_2H_4)_2H_8]_2(PtCl_6)_3$, crystallizing in golden yellow needles which decompose, however, on recrystallization.[2]

*Triethylene Triamine*, $N_3(C_2H_4)_3H_3$, boils with partial decomposition at about 216°, and forms, in strongly acid solution, well crystallizable salts containing three equivalents of acid. When only a weak acid solution is used, salts are formed which contain only two equivalents of acid, and, if the free base be added to this solution, salts containing a still smaller quantity are formed. The platinichloride $[N_3(C_2H_4)\ H_6]_2\ (PtCl_6)_3$, is tolerably soluble in water, and crystallizes in long golden-yellow needles. Besides this, another compound, $[N_3(C_2H_4)_3H_4]_2\ PtCl_6$, is known, crystallizing in large prisms.

*Triethylene Tetramine*, $N_4(C_2H_4)_3H_6$, is a thick syrup. Its platinum compound, $N_4(C_2H_4)_3H_{10}(PtCl_6)_2$, is a pale yellow amorphous almost insoluble precipitate.

[1] *Proc. Roy. Soc.* x. 104 and 596.
[2] *Ib.* x. 619; xi. 413.

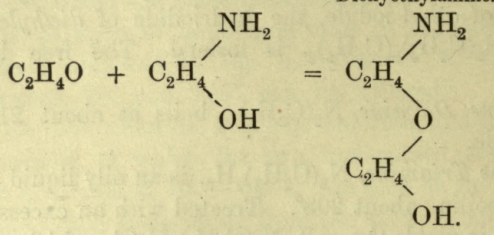
## Ethylene Oxide Bases.[1]

488 Ethylene oxide combines with aqueous ammonia with evolution of heat, when the following bases are formed:

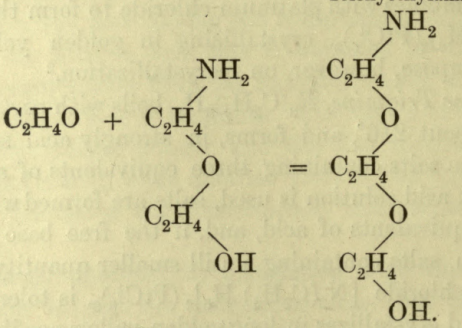
Oxyethylamine.

$$C_2H_4O + NH_3 = C_2H_4\begin{matrix}NH_2\\OH.\end{matrix}$$

Dioxyethylamine.



Trioxyethylamine.



These bodies remain on evaporation as syrupy liquids having a strong alkaline reaction. In order to separate them, they are neutralized with hydrochloric acid, evaporated, and the residue exhausted with absolute alcohol, when hydrochloride of trioxyethylamine remains behind. The solution is evaporated again to a syrup, and from this the salt of oxyethylamine is allowed gradually to crystallize and the crystals are then washed with alcohol. A more complete separation is effected by means of the platinichlorides. For this purpose a concentrated solution of platinum chloride is added to the alcoholic solution, when the salt of dioxyethylamine crystallizes out. Ether is then added to the mother-liquor, which precipitates some more of this salt,

[1] Wurtz, *Comptes Rendus*, xlix. 898; liii. 338; *Ann. Chem. Pharm.* cxiv. 51; xxi. 226.

until at last golden-yellow scales of the monoxyethylammonium platinichloride make their appearance. By decomposing these compounds with sulphuretted hydrogen, the hydrochlorides of the two bases are again formed. These are formed together when ethylene chlorhydrin is heated with ammonia to 100°.

The bases are obtained from the hydrochlorides by decomposition with silver oxide. They are thick strongly alkaline liquids which have not been further examined.

*Oxyethylammonium Chloride,* $C_2H_4(OH)NH_3Cl$, forms small crystals melting at 100°.

*Dioxyethylammonium Chloride,* $(C_2H_4)_2O(OH)NH_3Cl$, is very easily soluble in water and alcohol, and on the addition of platinum chloride deposits the platinichloride $[(C_2H_4)_2O(OH)NH_3]_2PtCl_6$, in large crystals resembling those of potassium dichromate.

*Trioxyethylammonium Chloride,* $(C_2H_4)_3O_2(OH)NH_3Cl$, crystallizes from water in large rhombohedrons.

When trioxyethylamine is warmed with ethylene oxide, higher *polyoxyethylamines* are formed, their basic properties decreasing with increase of oxygen. They have not been separated from one another, as neither they nor their salts crystallize.

Ethylene oxide and ethylene chlorhydrin combine together with amines to form oxy-bases or their hydrochlorides. Of these the following compounds have the greatest interest.

## CHOLINE AND NEURINE.

489 In the investigation of the constituents of ox and swine's bile Strecker discovered a base to which from analysis of its salts he gave the formula $C_5H_{13}NO$, and termed it *Choline,*[1] (χολή, bile). Liebreich at a later period obtained a basic compound as a decomposition-product of protagon, a body possessing a complicated constitution and forming the chief constituent of the materials of the brain and nerves. This basic substance he termed *Neurine* (νεῦρον, nerve),[2] and from analysis gave to it the formula $C_5H_{11}N$. The same compound was further investigated by Baeyer, who found that it is *oxyethyl-trimethyl-ammonium hydroxide,* $N(C_2H_4.OH)(CH_3)_3OH$. Hydriodic acid converts it into the compound $N(C_2H_4I)(CH_3)_3I$, and this when treated

[1] *Ann. Chem. Pharm.* cxxiii. 353. [2] *Ib.* cxxxiv. 29.

with silver oxide and water yields the vinyl base, $N(C_2H_3)(CH_3)_3OH$.[1] The same body was also obtained by Hofmann in a similar way from the corresponding bromine compound, which latter compound is obtained by the action of ethylene bromide on trimethylamine. Baeyer then suggested that neurine is probably identical with choline as well as with sincaline, a base formerly prepared by von Babo and Hirschbrunn as a product of decomposition of sinapin, a compound occurring in white mustard-seeds (sinapis alba).[2] The truth of this suggestion was soon afterwards proved by the investigations of Dybkowski,[3] and of Claus and Keese.[4]

Wurtz then prepared the base synthetically. He obtained the chloride by heating ethylene chlorhydrin with trimethylamine and prepared the base itself by bringing a concentrated solution of this amine together with ethylene oxide, and allowing the mixture to stand for a day :[5]

$$C_2H_4O + H_2O + N(CH_3)_3 = N(C_2H_4.OH)(CH_3)_3OH.$$

Further experiments of Liebreich then showed that the oxyethyl base is only formed when an alcoholic or ethereal extract of brain is used. Pure protagon on the other hand yields on boiling with baryta-water, the vinyl base to which he restricts the name of neurine, suggesting that the oxethyl base should be termed *Bilineurine*.[6]

*Choline, Bilineurine,* or *Oxyethyl-trimethyl-ammonium Hydroxide,* $N(C_2H_4OH)(CH_3)_3OH$, is formed as a decomposition-product of lecithin, a compound which will be described under Glycerin, and which occurs in gall, the yolk of egg, &c. The best method for preparing choline is according to Diakonow[7] to extract the yolk of egg repeatedly with ether and afterwards with warm alcohol. The ether and alcohol are afterwards distilled off, the residue boiled for an hour with baryta and the excess of baryta precipitated with carbon dioxide, and the filtrate evaporated. The residue is extracted with absolute alcohol, and the solution precipitated with platinum chloride. The precipitate is then dissolved in water, and the platinum

[1] *Ann. Chem. Pharm.* cxl. 306 ; cxlii. 322.
[2] *Ib.* lxxxiv. 10.
[3] *Journ. Prakt. Chem.* c. 151.
[4] *Ib.* cii. 24.
[5] *Ann. Chem. Pharm.* Suppl. vi.
[6] *Ber. Deutsch. Chem. Ges.* ii. 12.
[7] *Chem. Centralb.* 1868, 140, 169, 575.

thrown down with sulphuretted hydrogen. By the action of silver oxide on the choline hydrochloride thus obtained, a strongly alkaline solution of the free base is produced, and this, on evaporation, remains behind as a syrupy liquid.

*Oxyethyl-trimethyl-ammonium Chloride*, $N(C_2H_4OH)(CH_3)_3Cl$. Like most of the choline salts this is a deliquescent substance, crystallizing from absolute alcohol in fine needles. The platinichloride, $[N(C_2H_4OH)(CH_3)_3]_2PtCl_6$, crystallizes from hot water in orange-yellow rhombic prisms or tables, and is insoluble in alcohol. The aurichloride, $N(C_2H_4OH)(CH_3)_3AuCl_4$, is precipitated from the hot saturated aqueous solution in long yellow prisms. The sulphate is amorphous and very soluble in water but scarcely dissolves in absolute alcohol. The carbonate is very deliquescent, and also amorphous; it has an alkaline reaction, and its aqueous solution is not precipitated by alcohol. The *iodethyl-trimethyl-ammonium iodide*, $NC_2H_4I(CH_3)_3I$, has already been mentioned. It crystallizes from alcohol in large glistening imperfectly formed crystals resembling those of potassium iodide.

Choline is not only an ammonium hydroxide, but also an alcohol. On oxidation it is converted into *oxy-choline*, $N(CH_2.CO_2H)(CH_3)_3OH$, a body which will be described under the glycol compounds.

*Neurine*, or *Vinyl-trimethyl-ammonium Hydroxide*, $N(C_2H_3)(CH_3)_3OH$. This, as has been mentioned, was first discovered by Hofmann.[1] The free base is only known in aqueous solution, and has a strongly alkaline reaction. The platinichloride, $[N(C_2H_3)(CH_3)_3]_2PtCl_6$, is easily soluble in water, and crystallizes in yellow octohedrons, or in five-sided tables which soon become opaque, and then on solution in water leave a residue, whilst choline platinichloride remains in solution (Liebreich).

## PHOSPHORUS BASES OF ETHYLENE.

**490** The tertiary phosphines of the monad radicals act readily on ethylene bromide, giving rise to two series of compounds, the relative quantities of which depend upon the proportions in which the bodies are mixed. The compounds obtained from

[1] *Ann. Chim. Phys.* [3], liv. 356.

triethyl-phosphine will here only be described. With this, ethylene bromide yields the following bodies:[1]

$$P(C_2H_5)_3 + C_2H_4Br_2 = P(C_2H_4Br)(C_2H_5)_3\,Br.$$
$$2P(C_2H_5)_3 + C_2H_4Br_2 = P_2(C_2H_4)(C_2H_5)_6Br_2.$$

*Bromethyl-triethyl-phosphonium Bromide*, $P(C_2H_4Br)(C_2H_5)_3Br$, is formed by heating an ethereal solution of triethyl phosphine with excess of ethylene bromide. The product, which also contains the above-mentioned dibromide, is washed with ether, and crystallized from absolute alcohol. It is soluble in water and alcohol, and crystallizes in rhombic dodecahedrons. When its solution is treated with silver chloride, and platinum chloride added to the hot filtrate, long orange-yellow prisms of the compound $[P(C_2H_4Br)(C_2H_5)_3]_2PtCl_6$ are deposited.

*Oxyethyl-triethyl-phosphonium Hydroxide*, $P(C_2H_4OH)(C_2H_5)_3OH$, is obtained by boiling the bromide solution with silver oxide. The strongly alkaline solution dried over sulphuric acid yields a syrup. The base yields with acids well crystallizable salts. The hydroxide decomposes, on heating, into ethylene, water, and triethylphosphine. When treated with phosphorus pentachloride, the crystalline compound, *chlorethyl-triethyl-phosphonium chloride*, $N(C_2H_4Cl)(C_2H_5)_3Cl$, is formed.

*Vinyl-triethyl-phosphonium Compounds.* When bromethyl-triethyl-phosphonium bromide is boiled with water and silver acetate, and the silver bromide filtered off, and platinum chloride added to the concentrated solution, octohedrons of the vinyl salt, $[P(C_2H_3)(C_2H_5)_3]_2PtCl_6$, are deposited.

*Ethylene-hexethyl-phosphonium Dibromide*, $P_2C_2H_4(C_2H_5)_6Br_2$, is contained in the mother-liquor of the above monobromide. It is best obtained in the pure state by heating ethylene bromide with an excess of triethylphosphine. It crystallizes in white needles. Treated with silver oxide and water it yields a strongly alkaline hydroxide having a bitter taste, and drying in a vacuum to a syrupy mass. Its salts crystallize well. The chloride is very soluble in water, and crystallizes in large tables. The iodide is difficultly soluble in cold water, and separates from hot solution in fine white rhombic needles. As it crystallizes so easily, and therefore can be easily obtained pure, this salt is well suited for the preparation of other diphosphonium compounds. The platinichloride is almost insoluble in water, and separates from hot hydrochloric acid in monoclinic crystals.

[1] *Proc. Roy. Soc.* x. 100; *Ann. Chem. Pharm.* Suppl. i. 151.

## ARSENIC BASES OF ETHYLENE.

491 These compounds are closely allied to the foregoing phosphorus bases.

*Bromethyl-triethyl-arsonium Bromide*, $As(C_2H_4Br)(C_2H_5)_3Br$, is formed by heating ethylene bromide with triethylarsine. It crystallizes from hot water in rhombic dodecahedrons, and yields a finely crystalline platinichloride. By warming the monobromide with water and silver oxide a strongly alkaline solution of *vinyl-triethyl-arsonium hydroxide*, $As(C_2H_3)(C_2H_5)_3OH$, is obtained. The platinichloride of this body crystallizes in fine octohedrons.

*Ethylene-hexethyl-arsonium Dibromide*, $As_2C_2H_4(C_2H_5)_6Br_2$, is obtained when the above monobromide is heated with triethylarsine to 150°. It is converted by silver oxide and water into the hydroxide, the salts of which crystallize well.[1]

Hofmann has obtained, besides these, a large number of mixed ethylene bases containing nitrogen and phosphorus, nitrogen and arsenic, or phosphorus and arsenic. These bodies are very similar in their properties to those already described.[2]

## ETHIDENE OR ETHYLIDENE COMPOUNDS.

492 The radical *ethidene* or *ethylidene* does not exist in the free state. The oxide has already been described as acetaldehyde, $CH_3.CHO$, and it has been stated that the corresponding alcohol or ethidene glycol is not known, but that it probably exists in aqueous solution (p. 13). Trichlorethidene glycol, or chloral hydrate, is, however, known, together with a number of other ethidene and trichlorethidene compounds which are hereafter described.

*Ethidene Diethyl Ether*, or *Acetal*, $CH_3.CH(OC_2H_5)_2$. In examining the products of the slow combustion of alcohol over platinum-black Döbereiner found, amongst other products, a liquid to which he gave the name of heavy oxygen ether. This was afterwards investigated in 1833 by Liebig, who termed it *acetal*.[3] Stas then found that the same substance is formed when chlorine acts upon alcohol, and he it was who first gave to this

[1] Hofmann, *Proc. Roy. Soc.* xi. 62; *Ann. Chem. Pharm.* Suppl. i. 306.
[2] *Ib.* i. 289. [3] *Ann. Pharm.* v. 25; xiv. 156.

body its correct formula.[1] Its constitution was determined by Wurtz and Frapolli. They obtained it by treating aldehyde with phosphorus pentabromide, and by then acting upon the product, which according to their views (p. 72) contained ethidene bromide, with sodium ethylate.[2]

It is also formed by heating alcohol with aldehyde :[3]

$$CH_3.CHO + 2HO.C_2H_5 = CH_3.CH(OC_2H_5)_2 + H_2O.$$

This reaction takes place slowly in the cold, and hence acetal forms one of the constituents of crude spirit and is contained in the faints obtained in the process of rectification[4] (Part I. p. 295). According to Döbereiner it is also contained in old wine.

In order to prepare acetal, a mixture of two parts of alcohol, three parts of manganese dioxide, two parts of water, and three parts of sulphuric acid is distilled in a capacious flask until three parts have passed over, the distillate dried over chloride of calcium and rectified, and the portion boiling above 60° collected; this is again dried and then further rectified. On heating with strong caustic potash, the aldehyde and ethyl acetate, which it is difficult to separate from the acetal, are destroyed; then the whole is treated with fused calcium chloride, and lastly purified by fractional distillation.[5]

Acetal is a mobile liquid having a pleasant fresh smell and a nutty after-taste. It boils between 104° and 106°, and has at 22°·4 a specific gravity of 0·821. It is easily converted into aldehyde and acetic acid by means of oxidizing agents. When heated with acetic acid it is converted into ethyl acetate and aldehyde.[6]

Chlorine gives substitution-products similar to those which are obtained by the action of chlorine upon alcohol.

493 *Monochloracetal*, $CH_2Cl.CH(OC_2H_5)_2$, is not obtained pure in this way, as the substitution easily goes further. It is best prepared by treating dichlorether (Part I. p. 339) with sodium ethylate or absolute alcohol:

$$CH_2Cl.CHCl.OC_2H_5 + NaOC_2H_5 = CH_2Cl.CH(OC_2H_5)_2 + NaCl.$$

[1] *Ann. Chim. Phys.* [3], xix. 146.
[2] *Comptes Rendus*, xlvii. 418; *Ann. Chem. Pharm.* cviii. 223.
[3] Geuther and Alsberg, *ib.* cxxvi. 62.
[4] Krämer and Pinner, *Ber. Deutsch. Chem. Ges.* ii. 401.
[5] Wurtz, *Ann. Chem. Pharm.* c. 116; *Ann. Chim. Phys.* [3], xlviii. 370.
[6] Beilstein and Hofacker, *Ann. Chem. Pharm.* cxii. 239.

Monochloracetal is a pleasantly-smelling liquid boiling at 156°·8, and having a specific gravity of 1·0418 at 0°.[1] When heated with sodium the following reaction takes place :

$$CH_2Cl.CH(OC_2H_5)_2 + 2Na = CH_2{=}CH.OC_2H_5 + NaOC_2H_5 + NaCl.$$

*Vinyl-ethyl ether* thus obtained is a mobile liquid boiling at 35°·5, possessing a peculiar ethereal smell, and having at 14°·5 a specific gravity of 0·7625. It unites with chlorine again to form dichlorether, and it is decomposed by the action of dilute sulphuric acid into alcohol and aldehyde.[2]

*Dichloracetal*, $CHCl_2.CH(OC_2H_5)_2$, is formed easily, together with trichloracetal, by the action of chlorine upon alcohol (Lieben) and acetal.[3] It is an aromatic-smelling, oily liquid, boiling at 183°—184°, and having at 14° a specific gravity of 1·1383. When heated with sulphuric acid it forms dichloracetaldehyde, $CHCl_2.COH$, a heavy, mobile liquid, boiling at 88°—90°, and converted into acetylene tetrachloride by the action of phosphorus pentachloride.[4]

Trichloracetal will be described further on.

*Monobromacetal*, $CH_2Br.CH(OC_2H_5)_2$, is formed by the action of bromine upon acetal. It is a heavy not unpleasantly-smelling liquid boiling at 170° with partial decomposition.[5]

The above named vinyl-ethyl ether combines with bromine to form the dibrom-ether which decomposes on heating and which when heated with sodium ethylate yields monobromacetal.

By heating with alcoholic potash it is converted into *Hydroxyacetal*, $CH_2.OH.CH(OC_2H_5)_2$, a pleasantly-smelling liquid boiling at 167°. The ethyl ether, $CH_2(OC_2H_5)CH(OC_2H_5)_2$, corresponding to this alcohol, is formed when bromacetal is heated with sodium ethylate, and is a liquid boiling at 164°, and having an ethereal smell (Pinner).

*Ethidene-ethylene Dioxide*, $(C_2H_4)_2O_2$, is formed, according to Wurtz, when aldehyde is heated for several weeks with glycol to 100° :

[1] Lieben, *Ann. Chem. Pharm.* civ. 114 ; cxlvi. 193 ; Paternò and Mazzara, *Ber. Deutsch. Chem. Ges.* vi. 1202 ; Klien, *Jahresb.* 1876, 336.
[2] Wislicenus, *Ann. Chem. Pharm.* cxcii. 106.
[3] Pinner, *ib.* clxxix. 33 ; Krey, *Jahresb.* 1876, 474.
[4] Paternò, *Comptes Rendus*, lxvii. 456.
[5] Pinner, *Liebig's Ann.* clxxix. 33 ; Krey, *Jahresb.* 1876, 474.

$$\begin{matrix} CH_2.OH \\ | \\ CH_2.OH \end{matrix} + CHO.CH_3 = \begin{matrix} CH_2.O\diagdown \\ | \qquad CH.CH_3 \\ CH_2.O\diagup \end{matrix} + H_2O.$$

It is a pungent but not unpleasantly-smelling liquid, boiling at 82°·5, and at 0° having a specific gravity of 1·0002, whilst that of the vapour is 3·103.[1]

*Ethidene Methyl-ethyl Ether*, or *Methyl-ethyl Acetal*, $CH_3CH\begin{cases} OC_2H_5 \\ OCH_3 \end{cases}$, was obtained by Wurtz by oxidizing a mixture of alcohol and wood-spirit with manganese dioxide and sulphuric acid. It is a liquid smelling like common acetal, boiling at 85°, and having a specific gravity at 0° of 0·8535.

*Ethidene Dimethyl Ether*, or *Dimethyl Acetal*, $CH_3.CH(OCH_3)_2$, is formed together with the foregoing compound. It has a strong ethereal smell, boils about 65°, and at 0° has a specific gravity of 0·8556. Dancer found this compound in crude wood-spirit.[2]

## ETHEREAL SALTS AND ETHERS OF ETHIDENE.

494 *Ethidene Dichloride*, or *Dichlorethane*, $CH_3.CHCl_2$, was first prepared by Regnault by acting with chlorine upon ethyl chloride.[3] By treating aldehyde with phosphorus pentachloride both Geuther[4] and Wurtz[5] obtained a compound having the same composition but believed to be a body differing from Regnault's *éther hydrochlorique monochlorée*, until Beilstein[6] showed that the two are in reality identical. Ethidene chloride is also formed by the action of phosphorus chloride on paraldehyde.[7]

For the purpose of preparing it from ethyl chloride, the vapour of this substance is passed, mixed with chlorine, over animal charcoal heated to 250°—400°.[8] It is still more simply obtained by fractional distillation from the by-products of the chloral-manufacture.[9]

Ethidene chloride is an ethereal-smelling liquid having a sweet and biting taste. It boils at 59°·9, and at 0° has a specific

[1] *Comptes Rendus*, liii. 378; *Ann. Chem. Pharm.* cxx. 328.
[2] *Chem. Soc. Journ.* xvii. 222.
[3] *Ann. Chim. Phys.* [2], lxxi. 353.
[4] *Ann. Chem. Pharm.* cv. 321.
[5] *Compt. Rend.* xlv. 1013.
[6] *Ann. Chem. Pharm.* cxiii. 110.
[7] Geuther, *Zeitsch. Chem.* 1865, 24.
[8] Damoiseau, *Bull. Soc. Chim.* xxv. 113.
[9] Krämer, *Ber. Deutsch. Chem. Ges.* iii. 257.

gravity of 1·2044 (Thorpe). It is a very stable compound, and may be distilled without alteration over potassium. Heated with sodium to 200° chlorethylene, acetylene, ethane and ethylene are formed.[1] It is attacked by alcoholic potash with difficulty. Heated with sodium ethylate, it forms chlorethylene, $C_2H_3Cl$, and a little acetal. By the further action of chlorine it yields first *trichlorethane* or *dichlorethyl chloride*, $CH_3CCl_3$, and *monochlorethylene dichloride*, $CH_2Cl.CHCl_2$ (p. 41).[2] The first of these is a body resembling ethidene dichloride, boiling at 74°·5 and having at 0° a specific gravity of 1·3465. It is attacked by alcoholic potash only with difficulty on heating with formation of potassium chloride and potassium acetate:

$$\begin{matrix} CH_3 \\ | \\ CCl_3 \end{matrix} + 4KOH = \begin{matrix} CH_3 \\ | \\ CO.OK \end{matrix} + 3KCl + 2H_2O.$$

Higher chlorine substitution-products of these bodies have already been described (p. 42).

*Ethidene Dibromide*, $CH_3.CHBr_2$, was prepared by Hofmann[3] by heating ethyl bromide with bromine, and afterwards examined by Caventon,[4] Reboul,[5] and Tawildarow.[6]

It is formed also by the action of phosphorus bromochloride, $PBr_2Cl_3$, on aldehyde,[7] as well as by heating monobromethylene with hydrobromic acid (Reboul). It is a liquid which boils at 110°, and at 10° has a specific gravity of 2·129.

*Ethidene Di-iodide*, $CH_3.CHI_2$, is formed, according to Gustavson, when ethidene chloride is heated with a solution of aluminium iodide in carbon disulphide. It is a liquid boiling with decomposition at 177°—179°, and having a specific gravity of 2·84 at 0°.[8]

*Ethidene Chlorethylate*, $CH_3.CH\begin{cases} Cl \\ OC_2H_5 \end{cases}$, was obtained by Wurtz and Frapolli by passing a current of hydrochloric acid into a mixture of aldehyde and absolute alcohol. This compound is identical with monochlorether and by treatment with sodium ethylate is converted into acetal.

495 *Ethidene Oxychloride*, $(CH_3.CHCl)_2O$. This compound,

[1] Tollens, *Ann. Chem. Pharm.* cxxxvii. 311.
[2] Städel, *ib.* cxcv. 183.
[3] *Proc. Roy. Soc.* x. 619.
[4] *Compt. Rend.* lii. 1330.
[5] *Ib.* lxx. 398.
[6] *Ann. Chem. Pharm.* clxxvi. 12.
[7] Paternò and Pisati, *Ber. Deutsch. Chem. Ges.* v. 289.
[8] *Ib.* vii. 731.

metameric with dichlorether, was obtained by Lieben,[1] by the action of hydrochloric acid on well-cooled aldehyde. According to Geuther and Cartmell,[2] the compound $C_6H_{12}Cl_2O_2$ is first produced, and this may be considered to be paraldehyde in which one atom of oxygen is replaced by two of chlorine, and the following reaction taking place :

$$3CH_3.CHO + 2HCl = CH_3.CH\begin{matrix}\diagup OCHCl.CH_3 \\ \diagdown OCHCl.CH_3\end{matrix} + H_2O.$$

This body decomposes on distillation into aldehyde and ethidene oxychloride :

$$CH_3.CH\begin{matrix}\diagup OCHCl.CH_3 \\ \diagdown OCHCl.CH_3\end{matrix} = CH_3.CHO + O\begin{matrix}\diagup CHCl.CH_3 \\ \diagdown CHCl.CH_3.\end{matrix}$$

Ethidene oxychloride is a liquid boiling at 116°—117°, and having at 12° a specific gravity of 1·1376. When heated with water it decomposes into hydrochloric acid and aldehyde, and by the action of zinc-ethyl it is converted into secondary butyl oxide.[3]

*Ethidene Chloracetin*, $CH_3.CH\begin{cases}Cl \\ O.CO.CH_3\end{cases}$, was obtained by Wurtz, together with acetyl chloride, by the action of chlorine upon aldehyde.[4] Maxwell-Simpson prepared it also by heating aldehyde with acetyl chloride.[5] It is a liquid boiling at 120°—124°, having an aromatic smell, is lighter than water and only slowly decomposed by this liquid. It dissolves in dilute caustic potash with formation of aldehyde, potassium acetate and potassium chloride.

*Ethidene Bromacetin*, $CH_3.CH\begin{cases}Br \\ O.COCH_3\end{cases}$, was first prepared by Wurtz and Frapolli by treating aldehyde with phosphorus pentabromide, and was considered to be ethidene bromide until Tawildarow pointed out its true constitution, inasmuch as he obtained it by heating aldehyde with acetyl bromide.[6] It is formed according to the equation :

[1] *Ann. Chem. Pharm.* cvi. 336.
[2] *Ib.* cxii. 13.
[3] Kessel, *Ann. Chem. Pharm.* clxxv. 44.
[4] *Ann. Chim. Phys.* [3], xlix. 58.
[5] *Phil. Mag.* [4], xvii. 195.
[6] *Ann. Chem. Pharm.* clxxvi. 12.

$$2COH.CH_3 + PBr_5 = O\begin{cases} CO.CH_3 \\ CHBr.CH_3 \end{cases} + HBr + PBr_3.$$

It boils between 135° and 145° with partial decomposition.

*Ethidene Diacetate*, $CH_3.CH(OC_2H_3O)_2$, is formed by heating aldehyde with acetic anhydride,[1] to 180°, and when alcoholic solutions of potassium acetate and chloracetin are mixed together.[2] It is a liquid having a peculiar smell resembling onions, and boils at 168°·8, whilst its specific gravity at 12° is 1·061. It is only slowly decomposed by water; caustic potash decomposes it into aldehyde and acetic acid.

## Ethidene Sulphite Compounds.

496 In the year 1853 Bertagnini made the observation that benz-aldehyde unites with the acid sulphites of the alkali-metals to form crystalline difficultly-soluble compounds, and that the other aldehydes do the same.[3] Later on Limpricht found that many ketones yield similar compounds,[4] and as these bodies are easily decomposed by acids or alkalis with separation of the aldehyde or ketone, they are often employed for the purification of the latter bodies.

It remained doubtful whether common aldehyde yielded such compounds, until Bunte showed in 1873 that they exist, and gave to them the name of aldehyde sulphurous acid salts.[5] These are distinguished from those of the aldehydes having a higher molecular weight, inasmuch as they are very soluble in water, and as they decompose at 100° they can only be obtained by slow evaporation over sulphuric acid in an exsiccator. They may be looked upon as the salts of ethidene sulphurous acid.

*Potassium Ethidene Sulphite*, $CH_3.CH\begin{cases} OH \\ OSO_2K \end{cases}$ When aldehyde is added to a concentrated solution of hydrogen potassium sulphite a combination takes place with considerable evolution of heat. The salt crystallizes in hard microscopic radiating needles. *Sodium Ethidene Sulphite*, $CH_3\begin{cases} OH \\ O\,SO_2Na \end{cases} + H_2O$, crystallizes from water in fine laminæ having a fatty lustre, and is precipitated by alcohol in the form of glistening needles.

[1] Geuther, *Ann. Chem. Pharm.* cvi. 249.
[2] R. Schiff, *Ber. Deutsch. Chem. Ges.* ix. 304.
[3] *Ann. Chem. Pharm.* lxxxv. 179, 268.
[4] *Ib.* xciii. 238. [5] *Ib.* clxx. 305.

The *ammonium salt* appears only to exist in aqueous solution. On evaporation, small needles are obtained having the formula $C_2H_7NO_3S$; these are, therefore, probably the amide $CH_3.CH\begin{cases}OH\\O.SO.NH_2\end{cases}$. The same compound was also formerly obtained by Petersen by the action of sulphur dioxide on deliquesced aldehyde-ammonia.[1]

## COMPOUNDS OF ETHIDENE WITH NITROGEN.

497 *Ethidene Hydramine*, $CH_3.CH\begin{cases}OH\\NH_2\end{cases}$. This compound was first observed by Döbereiner, but investigated more closely by Liebig, who termed it *aldehyde-ammonia* (Vol. III. Part I. p. 476). When an ethereal solution of aldehyde is saturated with ammonia, crystals of this compound are deposited. These have an alkaline reaction, and are soluble in all proportions in water; they are also very soluble in alcohol but dissolve only slightly in ether. When ether is added to the alcoholic solution and this allowed to stand, transparent hard glassy rhombohedrons are deposited. These melt at 70°—80°, and may be distilled at 100°. The specific gravity of the vapour at 160° has been found to be 30·36,[2] compared with hydrogen as unity. Above 185° decomposition begins. Dilute acids decompose it with liberation of aldehyde. It is therefore much more unstable than its isomeride oxyethylamine (p. 62). It possesses a peculiar ammoniacal yet turpentine-like smell, and it is decomposed in contact with air, especially in presence of light, becoming first yellow, then brown, and after a time deliquescing. On heating it evolves a smell like that of burning animal matter. On passing sulphur dioxide into its aqueous solution Redtenbacher[3] obtained small needles of the compound $C_2H_7NO_3S$, which is isomeric with taurine, and with the above named ethidene sulphamide. This body is much more easily soluble in water than the last compound, and much less stable. It decomposes when heated to 100° (Bunte), and on recrystalliza-

[1] *Ann. Chem. Pharm.* cii. 317.
[2] Schröder, *Ber. Deutsch. Chem. Ges.* iv. 470.
[3] *Ann. Chem. Pharm.* lxv. 40.

tion. Its constitution is probably represented by one of the following formulæ:

$$CH_3.CH\begin{cases} OH \\ NH.SO_2H. \end{cases} \qquad CH_3.CH\begin{cases} O— \\ NH_3 \end{cases}\!\!>SO_2.$$

*Ethidene Imido-Silver Nitrate*, $2(CH_3\,CH.NH)_2AgNO_3 + H_2O$, was first prepared by Liebig,[1] and its composition was ascertained by Liebermann and Goldschmidt,[2] and by Mixter.[3] It is obtained when an ammoniacal alcoholic solution of aldehyde is precipitated by silver nitrate. The crystalline precipitate is not very soluble in water, and deposits a metallic mirror on boiling. If this compound be dissolved in ammonia and allowed to evaporate in a vacuum over sulphuric acid, it separates in monoclinic crystals.

Silver sulphate gives a variety of crystalline compounds with aldehyde-ammonia.[4]

An alcoholic solution of aldehyde-ammonia undergoes alteration when allowed to stand for some time, and this takes place quickly on heating, a series of bodies being formed to which the name of *aldehyde bases* or *aldines* has been given, and of which the following have been described:

Hydracetamide, $C_6H_{12}N_2$
Oxytrialdine, $C_6H_{11}NO$.
Oxytetraldine, $C_8H_{13}NO$.
Oxypentaldine, $C_{10}H_{15}NO$.

These bodies are amorphous, and form salts of which only a few are characteristic.[5]

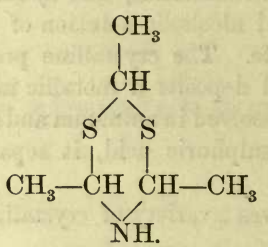
498 *Thialdine*, $C_6H_{13}NS_2$, was discovered in 1847 by Wöhler and Liebig, who obtained it by the action of sulphuretted hydrogen on an aqueous solution of aldehyde-ammonia.[6] It crystallizes from ether containing alcohol in large highly-refracting monoclinic prisms (Rammelsberg) melting at 43°, and having a peculiar aromatic smell, which after a time becomes unpleasant. It volatilizes slightly at the ordinary temperature, and is readily volatile in aqueous vapour. When heated by itself it undergoes decomposition. It is a monacid base. Its salts

[1] *Ann. Pharm.* xiv. 146.
[2] *Ber. Deutsch. Chem. Ges.* x. 2179; xi. 1198.
[3] *Sillim. Amer. Journ.* [3], xiv. 195.
[4] Mixter, *ib.* [3], xvii. 427.
[5] Schiff, *Ann. Chem. Pharm.* Suppl. vi. 1; Von Babo, *Journ. Prakt. Chem.* lxxii. 88; Heintz and Wislicenus, *Pogg. Ann.* cv. 577.
[6] *Ann. Chem. Pharm.* lix. 296.

crystallize well, and have been investigated by Wöhler and Liebig,[1] as well as by Brusewitz and Cathander.[2]

*Methyl-thialdine Hydriodide*, $C_6H_{12}(CH_3)NS_2,HI$, is a crystalline body obtained by the action of methyl iodide on thialdine. It is slightly soluble in water, and dissolves more readily in alcohol.[3]

Thialdine has probably the following constitution:



*Selenaldine*, $C_6H_{13}NSe_2$, is obtained by the action of seleniuretted hydrogen on a solution of aldehyde-ammonia. It forms small crystals, and the solution gradually decomposes on exposure (Wöhler and Liebig).

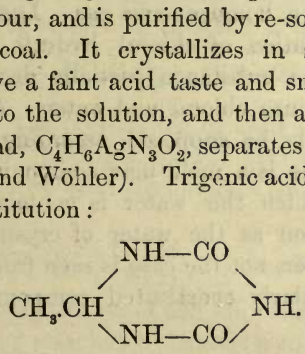
*Carbothialdine* or *Diethidene-ammonium Thiocarbamate*, $CS\begin{cases}NH_2\\SN(CH.CH_3)_2\end{cases}$, separates out in glistening white crystals on evaporating sulphide of carbon with an alcoholic solution of aldehyde-ammonia. These are difficultly soluble in alcohol, and scarcely soluble in water.[4] It is also formed by the action of aldehyde-ammonia on ammonium thiocarbamate.[5] It acts as a weak base. Its solution in hydrochloric acid easily decomposes, with formation of sal-ammoniac, aldehyde, and carbon disulphide. If its solution be treated with ferric chloride, ferric thiocyanate is formed slowly in the cold but quickly on warming. If, however, hydrochloric acid be present, then not only ferrous chloride and aldehyde are formed, but a white crystalline powder is thrown down, having the composition $S_2(CS.NH_2)_2$.[6] This is identical with the compound discovered by Zeise, and termed *hydranzothin*, obtained by him by acting upon ammonium thiocyanate with chlorine water or a mixture of hydrochloric acid and ferric chloride.[7]

[1] *Ann. Chem. Pharm.* lxi. 1. [2] *Journ. Prakt. Chem.* xcviii. 315.
[3] Hofmann, *Ann. Chem. Pharm.* ciii. 93.
[4] Liebig and Redtenbacher, *ib.* lxv. 43.
[5] Mulder, *ib.* clxviii. 235.
[6] Guareschi, *Ber. Deutsch. Chem. Ges.* xi. 1383.
[7] *Ann. Chem. Pharm.* xlvii. 36.

499 *Ethidene Acetamide*, $CH_3.CH(NH.C_2H_3O)_2$, is formed by heating aldehyde with acetamide. It crystallizes in large prisms, which are decomposed by acids with formation of aldehyde.[1]

*Ethidene Cyanuramide*, $C_3N_3(N.CH.CH_3)_3 + H_2O$, is obtained by the action of cyanamide on aldehyde. It forms a resinous mass, which is precipitated from alcoholic solution by chloroform in scales. It is insoluble in bisulphide of carbon, and possesses the same coefficient of refraction as that liquid, and for this reason it cannot be seen when it is suspended in it.[2]

*Ethidene-Biuret*, $C_4H_7N_3O_2$, was discovered by Wöhler and Liebig, and obtained by passing the vapours of cyanic acid into aldehyde. It was first called trigenic acid, probably because it contained three molecules of cyanic acid. The action of these bodies on one another is extremely energetic; carbon dioxide is evolved with almost explosive violence unless ice be added. The cyanic acid in the latter case is, however, but slowly absorbed, and then if the liquid be allowed to remain at the ordinary temperature, a quiet evolution of carbon dioxide takes place, which, like that of a fermenting liquid, lasts for some days, until at last the half-solidified mass forms a syrup from which crystals are deposited. The product, which contains cyamelide (Vol. I. p. 671) and aldehyde-ammonia, is boiled with hydrochloric acid until aldehyde is evolved. It is then filtered off, when on cooling trigenic acid separates out. It has a slightly yellow colour, and is purified by re-solution and warming with animal charcoal. It crystallizes in small white stellar needles, which have a faint acid taste and smell. When silver nitrate is added to the solution, and then ammonia gradually, the silver compound, $C_4H_6AgN_3O_2$, separates out as a crystalline powder [3] (Liebig and Wöhler). Trigenic acid probably possesses the following constitution:



[1] Tawildarow, *Ber. Deutsch. Chem. Ges.* v. 477.
[2] Knop, *Ann. Chem. Pharm.* cxxxi. 253.
[3] *Ib.* lix. 296.

## COMPOUNDS OF TRICHLORETHIDENE.

500 *Trichlorethidene Alcohol*, $CCl_3.CH(OH)_2$, has already been described as *chloral hydrate* (Vol. III. Part I. p. 539). This body is obtained by the union of chloral (trichlorethidene oxide) with water. Although it appears to undergo no change on distillation, it is converted by heating into its constituents, as is proved by the specific gravity of its vapour. Various chemists have, however, questioned this fact; and it has been the subject of a lively discussion in which the question of the constitution of this chloral hydrate was of less consequence than the question of the truth of the general applicability of Avogadro's law, according to which equal volumes of different gases contain, at the same temperature and pressure, equal numbers of molecules.[1]

The result of this experimental discussion has been to prove that the vapour of chloral hydrate is a mixture. That this is the case is shown by the following facts. In the first place Wurtz found that the vapours of chloral and water may be brought together without any evolution of heat being noticed, and hence undergo no chemical combination.[2] Then Wiedeman and Schulze[3] showed that the vapour of the hydrate when allowed to diffuse, behaved as a mixture of aqueous vapour and chloral vapour, and not as a homogeneous gas. Lastly Naumann has proved the dissociation of chloral hydrate, inasmuch as he has shown that the substance partially decomposes, on fractional distillation, into chloral and water. According to these facts, then, it might be supposed, according to the old idea, that chloral hydrate is a molecular compound, that is to say, a compound in which the water is contained in the same state of combination as the water of crystallization in salts. That this is, however, not the case is seen from the reactions of the following similarly constituted compounds and of other bodies.

*Trichlorethidene Ethyl Ether*, $CCl_3.CH\begin{cases} OH \\ OC_2H_5 \end{cases}$. This body, which is usually termed *Chloral Alcoholate*, is, as has been stated, the last product of the action of chlorine upon alcohol (Vol. III. Part I. p. 538), and is formed with evolution of heat when

[1] Vol. I. 38-70. [2] *Compt. Rend.* lxxxix. 190.
[3] *Pogg. Ann.* [2] vi. 293.

chloral and alcohol are brought together. It is difficultly soluble in cold water, but dissolves readily in alcohol, and crystallizes in white prisms which according to Liebig melt at 46°, but according to Jacobsen at 56°. It boils at 115°—116°, decomposing into chloral and alcohol, as is shown by the specific gravity of the vapour, which is 3·49,[1] and hence it behaves like chloral hydrate. That it is not, however, a molecular compound in which the alcohol plays the part of water of crystallization has been shown by Henry. If the supposition were correct, it must, when treated with phosphorus pentachloride, decompose into a mixture of pentachlorethane and ethyl chloride, whereas tetrachlorether is in fact formed.[2]

Chloral not only combines with common alcohol, but also with other alcohols, with mercaptan, with the glycols, with chlorhydrins,[3] &c.

*Trichlorethidene Diethyl Ether* or *Trichloracetal* exists in the two following modifications:

$$H\text{CCl}_2.\text{CCl}(\text{OC}_2\text{H}_5)_2. \qquad \text{CCl}_3.\text{CH}(\text{OC}_2\text{H}_5)_2.$$

The first of these is formed by the continued action of chlorine upon alcohol or acetal, and crystallizes from alcohol in white monoclinic prisms melting at 83°, and volatilizing in the vapour of water, and boiling with slight decomposition at 230°.[4]

The second compound was discovered by Wurtz and Vogt, who obtained it by heating tetrachlorether and alcohol together:[5]

$$\text{CCl}_3.\text{CHCl}(\text{OC}_2\text{H}_5) + \text{HO}.\text{C}_2\text{H}_5 = \text{CCl}_3.\text{CH}(\text{OC}_2\text{H}_5)_2 + \text{HCl}.$$

It is also formed in the preparation of chloral,[6] and is a liquid boiling at 204°·8, and having a specific gravity at 0° of 1·2813.[7] Concentrated sulphuric acid decomposes it with evolution of chloral.

*Pentachloracetal*, $\text{CCl}_3.\text{CH}\left\{\begin{matrix}\text{OC}_2\text{H}_5\\ \text{OC}_2\text{H}_3\text{Cl}_2\end{matrix}\right.$, was found by Friedel in the residues of the preparation of chloral. It is a liquid boiling at 186°—189°, and is not attacked by caustic potash. When heated

[1] *Ber. Deutsch. Chem. Ges.* iii. 909.
[2] *Ib.* iv. 101 and 435.
[3] Martius and Mendelssohn, *ib.* iii. 445; Henry, *ib.* vii. 762; Jacobsen, *Ann. Chem. Pharm.* clvii. 243.
[4] Paternò, *ib.* cl. 253; Krey, *Jahresb.* 1876, 474.
[5] *Compt. Rend.* lxxiv. 777.
[6] Lieben, *Ann. Chem. Pharm.* civ 114: Byasson, *Compt. Rend.* lxxvii. 26.
[7] Paternò and Pisati, *Jahresb.* 1872, 303.

with solid caustic potash, the compound $CCl_2 = C \begin{cases} OC_2H_5 \\ OC_2H_3Cl_2 \end{cases}$ is obtained, boiling between 153° and 159°.[1]

*Trichlorethidene Ethyl Acetin*, $CCl_3.CH \begin{cases} OC_2H_5 \\ OC_2H_3O \end{cases}$, is formed by acting upon acetyl chloride with chloral-alcoholate, and it is a pleasantly smelling liquid boiling at 198°, and having at 11° a specific gravity of 1·327.[2]

*Trichlorethidene Chloracetin*, $CCl_3.CH \begin{cases} Cl \\ OC_2H_3O \end{cases}$, is obtained by the action of acetyl chloride on chloral or chloral hydrate. It is a liquid boiling at 185°, and having at 17° the specific gravity 1·4761 (Meyer and Dulk).

*Trichlorethidene Diacetate*, $CCl_3.CH(OC_2H_3O)_2$, is obtained by heating together chloral and acetic anhydride for many hours to 150°. It is a peculiarly smelling liquid, boiling at 221°—222°. and having a specific gravity of 1·422 at 11° (Meyer and Dulk).

501 *Trichlorethidene Sulphite Compounds.* Like other aldehydes, chloral also combines with the acid sulphites of the alkali-metals to form crystalline compounds. The potassium salt, $C_2Cl_3H(OH)SO_3K$, crystallizes in glistening laminæ,[3] difficultly soluble in cold water. This salt is also formed when the normal sulphate is used, but the solution must then not be warmed, as compounds free from chlorine are then produced.[4]

*Trichlorethidene Thiohydrin*, $(CCl_3.CH.OH)_2S$, is formed by the action of sulphuretted hydrogen on an ethereal solution of chloral, or on an aqueous one of chloral hydrate. It is insoluble in water, crystallizes from chloroform in rhombohedrons, has a peculiar mercaptan-like smell, and melts at 127°—128°, with partial decomposition.[5]

*Trichlorethidene Hydramine*, $CCl_3.CH \begin{cases} OH \\ NH_2 \end{cases}$. This body, commonly called *chloral-ammonia*, is formed by the action of ammonia on well-cooled chloral.[6] In order to prepare it, chloral is dissolved in chloroform, and ammonia led into this liquid, well cooled in a mixture of ice and common salt.[7] It crystallizes in white needles which melt at 62°—64°. It is almost insoluble in

[1] *Ber. Deutsch. Chem. Ges.* viii. 642.
[2] Meyer and Dulk, *Ann. Chem. Pharm.* clxxi. 69.
[3] Städeler, *ib.* cvi. 253. [4] Rathke, *ib.* clxi. 154.
[5] Hagemann, *Ber. Deutsch. Chem. Ges.* v. 154; Wyss, *ib.* vii. 211.
[6] Städeler, *loc. cit.*; Personne, *Ann. Chem. Pharm.* clvii. 113.
[7] R. Schiff, *Ber. Deutsch. Chem. Ges.* x. 165.

cold water, and hot water decomposes it with formation of chloroform and ammonium formate.

*Trichlorethidene Ethylhydramine*, $CCl_3.CH\left\{\begin{matrix}OH\\N(C_2H_5)H,\end{matrix}\right.$ is formed by the action of anhydrous ethylamine on chloral. A white crystalline mass is thus produced, which, on heating, decomposes into chloroform and ethyl formamide [1] (Vol. III. Part I. p. 406).

*Trichlorethidene Hydracetamide*, $CCl_3.CH\left\{\begin{matrix}OH\\N(C_2H_3O)H\end{matrix}\right.$ Acetamide and chloral combine together with evolution of heat-giving rise to the above-named body.[2] It also occurs when chloral-ammonia is treated with acetyl chloride (Schiff). It crystallizes from hot water in rhombic tables, which melt at 156°. When heated with acetyl chloride for some hours to 120°, the compound, $CCl_3.CH\left\{\begin{matrix}OC_2H_3O\\N(C_2H_3O)H,\end{matrix}\right.$ is formed. This crystallizes from hot acetic acid in transparent prisms, which melt at 117°—118°, and are decomposed by hot water into the foregoing compound and acetic acid (Schiff).

*Trichlorethidene Diacetamide*, $CCl_3.CH\left\{\begin{matrix}N(C_2H_3O)H\\N(C_2H_3O)H,\end{matrix}\right.$ is formed by heating chloral with acetonitril. It is difficultly soluble in water and alcohol, and crystallizes from acetic acid in glistening needles, which, when heated, sublime without previous fusion.[3]

*Trichlorethidene Urea*, $CO\left\{\begin{matrix}NH_2\\NH.CH(OH)CCl_3\end{matrix}\right.$ This substance is formed by the action of chloral on a solution of urea. It forms hard rhombic crystals, easily soluble in hot water. When an excess of chloral is added to a saturated solution of urea, the compound, $CO\left\{\begin{matrix}NH.CH(OH)Cl_3\\NH.CH(OH)Cl_3,\end{matrix}\right.$ insoluble in water, is produced. This crystallizes from alcohol in small six-sided tables, or in large flat pearly needles.

The amido-compounds of trichlorethidene are not attacked by dilute acids, but are easily decomposed by alkalis, with formation of the same products as are yielded by the substances from which they have been obtained. Thus, for example, the acetamide compound yields chloroform, ammonia, potassium formate, and potassium acetate (Jacobsen).

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 247.
[2] Jacobsen, *Ann. Chem. Pharm.* clvii. 244; Wallach, *Ber. Deutsch. Chem. Ges.* v. 251. [3] Hübner, *ib.* vi. 109; Hepp, *ib.* x. 1651.

## THE GLYCOLYL COMPOUNDS.

### Glycollic Acid or Oxyacetic Acid, $CH_2(OH)CO_2H$.

**502** This substance was obtained by Strecker in 1848, by acting with nitrogen trioxide on glycocoll (amido-acetic acid).[1] It was afterwards more carefully examined by himself and Socoloff, having been prepared by them from hippuric acid (benzoyl amido-acetic acid).[2] Although Strecker must be looked upon as the discoverer of glycollic acid, it is interesting to learn that so early as the year 1806 it had been noticed by Berzelius, who found it in the acid residues obtained in the preparation of ethyl nitrite by Black's method (Part I. p. 357). He, however, thought that this acid was malic acid. The next step in the history of glycollic acid was made by Debus, who showed that it is produced together with oxalic acid, its aldehyde, and other products by the moderate action of dilute nitric acid on alcohol.[3] Wurtz then obtained this acid by the oxidation of ethylene alcohol,[4] and Kekulé found that it can be readily prepared by heating aqueous potassium chloracetate.[5]

Glycollic acid also occurs in unripe grapes, but it disappears during the process of ripening,[6] being, in all probability, transformed into tartaric acid. It is also found in the green leaves of the Virginian creeper.[7]

Debus's method for preparing glycollic acid has been improved by Lautemann[8] and Drechsel.[9] Instead of exposing alcohol to gradual oxidation with nitric acid, it is better to use the mother-liquors from the manufacture of fulminating mercury. Cloëz was the first to observe that an acid occurs in this liquid, to which he gave the name of homolactinic acid.[10] Dessaignes suggested that this was glycollic acid,[11] an idea confirmed afterwards by Fahlberg.[12] According to this latter authority, the mother-liquor contains at first little or no glycollic acid, but this is formed in large quantity when the liquid is allowed to stand for some time at a temperature of 25°. The mercury which is still

[1] *Ann. Chem. Pharm.* lxviii. 55. [2] *Ib.* lxxx. 34. [3] *Ib.* c. 1.
[4] *Comptes Rendus*, xliv. 1306; *Ann. Chem. Pharm.* ciii. 367. [5] *Ib.* cv. 286.
[6] Erlenmeyer and Hoster, *Jahresb.* 1864, 359; *ib.* 1866, 373.
[7] Gorup Besanez, *Ann. Chem. Pharm.* clxi. 229.
[8] Kolbe, *Lehrb. Org. Chem.* i. 678.
[9] *Ann. Chem. Pharm.* cxxvii. 150. [10] *Ib.* lxxxiv. 282.
[11] *Ib.* lxxxix. 339. [12] *Journ. Prakt. Chem.* vii. 329.

contained in solution is then thrown down by sulphuretted hydrogen, a large excess of milk of lime added to the filtrate, this boiled and filtered hot, and the filtrate treated with carbon dioxide in order to separate the lime. On concentrating the solution, calcium glycollate is obtained, and this can be purified by recrystallization. In order to obtain the free acid, the lime salt is decomposed by an excess of oxalic acid and the boiling liquid saturated with lead carbonate, the solution of the lead salt precipitated by sulphuretted hydrogen, and the acid solution filtered off from the lead sulphide.

The two glucoses, dextrose and levulose, are easily oxidized in aqueous solution by silver-oxide, with formation of carbon dioxide, glycollic acid, and oxalic acid. This reaction may be employed for the preparation of glycollic acid. For this purpose a mixture of the two glucoses is prepared by boiling one part of cane sugar with twenty parts of a 2 per cent. sulphuric acid for two hours with a reversed condenser, and then removing the sulphuric acid by barium carbonate. The filtrate is added to a warm moist mixture of two parts of calcium carbonate and the oxide prepared from ten parts of silver nitrate. After a few minutes an evolution of carbon dioxide begins, and as soon as this has ceased, the mixture is warmed to 50° as long as any gas is evolved. It is then filtered, and the glycollate allowed to crystallize. One hundred parts of sugar give thirty parts of the dry salt. The addition of calcium carbonate at the commencement of the operation serves the purpose of keeping the solution neutral, as, if it becomes acid, the glycollic acid is readily further oxidized to oxalic acid.[1]

503 Glycollic acid may also easily be obtained from monochloracetic acid, as, on boiling this with caustic soda, sodium glycollate is formed:

$$CH_2Cl.CO_2Na + NaOH = CH_2(OH)CO_2Na + NaCl.$$

A concentrated solution of sulphate of copper is added to the hot solution, and the difficultly soluble copper glycollate thrown down. This may be purified by recrystallization, and decomposed by sulphuretted hydrogen.

According to Fittig, glycollic acid is most easily prepared by heating a 5 per cent. solution of chloracetic acid for some days in connection with a reversed condenser, and concentrating the product by evaporation.[2]

[1] Kiliani, *Ann. Chem. Pharm.* ccv. 191. [2] Liebig's *Annalen*, ccv. 191.

Glycollic acid separates from syrupy solution in stellated needles, and from solution in alcohol or ether in fine laminæ, which melt at 80°, and are unalterable in the air. If the aqueous solution be evaporated too far, some glycollic anhydride, a body which will be afterwards described, is formed, and if it be crystallized from alcoholic ether, some ethyl glycollate is also produced. Both of these products either prevent the crystallization of the acid, or render it deliquescent in moist air, and hence it was formerly assumed that two isomeric glycollic acids exist.[1]

By the action of phosphorus pentachloride on glycollic acid, glycolyl chloride is formed, a body which has been already described as monchloracetyl chloride (Part I. p. 535).

## The Glycollates.

504 The salts of oxyacetic acid are easily soluble in water, and crystallizable. Of these the following are the most characteristic.

*Calcium Glycollate*, $(C_2H_3O_3)_2Ca$, crystallizes by spontaneous evaporation of its solution in stellar silky needles, containing 4 molecules of water, and dissolving at 15° in 80 and at 100° in 19 parts of water. It separates from the hot solution on cooling in crystals which contain 3 molecules of water, and on evaporating at 100° large transparent hard crystals are obtained, which are only soluble with difficulty in water.

*Lead Glycollate*, $(C_2H_3O_3)_2Pb$, is obtained from acid solution in glistening monoclinic crystals, which dissolve at 17° in 31 parts of water. When the neutral solution is boiled, or if a glycollate be precipitated with acetate of lead, a basic salt, having the formula $(C_2H_3O_3Pb)_2O$, separates out in stellar needles which require more than 10,000 parts of water to dissolve them.

*Copper Glycollate*, $(C_2H_3O_3)_2Cu$, forms blue crystals, which dissolve in 134 parts of cold, and are more easily soluble in hot, water.

*Silver Glycollate*, $C_2H_3O_3Ag$, is a curdy precipitate, which after a time becomes crystalline. It dissolves in hot water, with partial decomposition and blackening.

[1] Kolbe, *Ann. Chem. Pharm.* cxxvii. 159.

## Ethers and Ethereal Salts of Glycolyl.

505 *Ethyl Glycollate*, $C_2H_3O_3(C_2H_5)$, is formed by heating ethyl chloracetate with anhydrous sodium acetate and alcohol : [1]

$$CH_2Cl.CO_2C_2H_5 + C_2H_3O_2Na + C_2H_5.OH =$$
$$CH_2(OH)CO_2C_2H_5 + C_2H_3O_2(C_2H_5) + NaCl.$$

In place of sodium acetate, sodium glycollate may be used when of course no ethyl acetate is formed.[2]

It may be more readily obtained by distilling a mixture of calcium glycollate and potassium ethyl sulphate (Fahlberg).

It is a pleasantly smelling liquid, soluble in water, and decomposing quickly in contact with this liquid, especially on heating, into glycollic acid and alcohol. According to Heintz it boils at 155°, whilst Fahlberg gives the boiling point at 150°, and Schreiner at 160°. At 0° it has a specific gravity of 1·1074.

The following ethers have also been prepared : [3]

| | B.P. | Sp. Gr. at 0°. |
|---|---|---|
| Methyl glycollate, $C_2H_3O_3(CH_3)$ | 151° | 1·1862 |
| Propyl glycollate, $C_2H_3O_3(C_3H_7)$ | 170° | 1·0837 |

*Ethyl-glycollic Acid*, $CH_2(OC_2H_5)CO_2H$. This body, isomeric with ethyl glycollate, is also termed *oxyethylacetic acid* and *ethoxacetic acid*. In order to prepare it 30 grams of sodium are dissolved in 500 grams of absolute alcohol, and an alcoholic solution of 60 grams of chloracetic acid added to it, and the whole heated to boiling. The liquid is filtered from the sodium chloride which separates out, the alcohol removed by distillation, and the residue warmed with 69 grams of copper sulphate. The residue, obtained on evaporation, is a mixture of sodium sulphate and copper ethyl-glycollate, $[C_2H_2(C_2H_5)O_3]_2Cu + 2H_2O$, from which the latter salt is obtained on extraction with hot alcohol, it separating out on cooling in small blue needles. It is easily soluble in water, and crystallizes in large rhombic prisms. On treating its aqueous solution with sulphuretted hydrogen and distilling the filtrate, ethyl-glycollic acid passes over at about 190°, this being mixed with a small quantity of glycollic acid, paraformaldehyde, and ethyl-glycollic ethyl ether. It is a colourless, strongly acid liquid boiling at from 206°—207°

[1] Heintz, *Ann. Chem. Pharm.* cxxiii. 325. [2] *Pogg. Ann.* cxiv. 440.
[3] *Ann. Chem. Pharm.* cxcvii. 1.

(Henry). On heating it with phosphorus iodide, glycollic acid and ethyl iodide are formed.[1] Phosphorus trichloride does not attack it in the cold, but, on heating, ethyl-glycolyl chloride is formed, $CH_2(OC_2H_5)COCl$. This is a mobile, heavy liquid, boiling at 127°—128°, fuming slightly in the air, and attacking the eyes violently.[2]

*Ethyl Ethoxacetate*, $CH_2(OC_2H_5)CO_2(C_2H_5)$, is obtained by heating sodium ethyl-glycollate with ethyl iodide and alcohol,[3] as well as by allowing ethyl chloracetate to drop into an alcoholic solution of sodium ethylate.[4] The ether, obtained by fractional distillation, is an easily mobile liquid, having a pleasant mint-like smell and a sweetish taste. It boils at 158°·4, and at 0° has a specific gravity of 0·9996, that of its vapour being 4·56.

In addition to these, many other compounds[5] and ethers (Schreiner) having an analogous constitution to ethyl-glycollic acid are known.

*Acetoglycollic Acid*, or *Acetoxacetic Acid*, $CH_2O(C_2H_3O).CO_2H$, is not known in the free state. Its ethyl ether is formed by heating ethyl chloracetate with anhydrous sodium acetate. It is a liquid having a faint fruit-like smell, and boiling at 179°. When it is treated in the cold with milk of lime, it forms the easily soluble *calcium acetoglycollate*, $(C_4H_5O_2)_2Ca + 2H_2O$, crystallizing in small prisms, and yielding on boiling with milk of lime the calcium salts of acetic and glycollic acids.[6]

The hydrogen in the alcoholic hydroxyl of glycollic acid may be replaced by other acid radicals, and in these cases also the ethers and salts but not the free acids are known.[7]

As glycollic acid is at once an alcohol and an acid, two molecules of it can unite with elimination of water and formation of compound ethers (p. 84).

506 *Glycoglycollic Acid*, $CH_2(OH)CO_2.CH_2.CO_2H$. This compound, which is at the same time an acid, an alcohol, and an ether, is usually called *glycollic anhydride*. It is formed on heating glycollic acid, or by exposing this for many days to the

[1] Heintz, *Pogg. Ann.* cix. 331 ; cxi. 552 ; cxiv. 469.
[2] Henry, *Ber. Deutsch. Chem. Ges.* ii. 276.
[3] Heintz, *Ann. Chem. Pharm.* cxxix. 39 ; Geuther and Wackenroder, *Zeitsch. Chem.* 1867, 705.
[4] Schreiner, *loc. cit.*
[5] Heintz, *loc. cit.* and *Ann. Chem. Pharm.* cxxx. 257 ; *Journ. Prakt. Chem.* lxxviii. 124, 174 (?) ; lxxix. 233 ; Siemens, *Chem. Centralb.* 1862, 17.
[6] Heintz, *Ann. Chem. Pharm.* cxxiii. 325 ; Gal, *ib.* cxlii. 370 ; *Comptes Rendus*, lxiii. 1086.
[7] Heintz, *Ann. Chem. Pharm.* cliv. 257 ; Gal, *loc. cit.*

action of the vapours of sulphur trioxide. On washing it with water it remains as a white powder which is insoluble in ether, alcohol, and cold water, whilst on boiling it forms glycollic acid. It is also dissolved by fused glycollic acid, and this explains the fact, noted on page 84, of the anomalous behaviour of fused glycollic acid (Fahlberg).

*Glycolide*, $C_4H_4O_4$, was first prepared by Dessaignes by the dry distillation of tartronic acid, $CH(OH)(CO_2H)_2$.[1] It is also formed on strongly heating glycollic acid, but most readily by heating potassium monochloracetate to 150°.[2]

$$\begin{array}{l} CH_2Cl \\ | \\ CO.ONa \end{array} + \begin{array}{l} NaOCO \\ | \\ ClCH_2 \end{array} = \begin{array}{l} CH_2—O—CO \\ | \qquad\quad | \\ CO—O—CH_2 \end{array} + 2NaCl.$$

It is also formed by the action of bromacetylbromide on sodium acetate.[3] It is a white amorphous powder, insoluble in cold water, melting at 220°, and combining with water to form glycollic acid, and with alcohol to form the ether.

Glycolide, as is seen from its mode of formation, is a double ether in which the radical glycolyl is contained twice, and both of these act at once as alcohol radicals and as acid radicals.

*Diglycollic Acid*, $O(CH_2.CO_2H)_2$. This dibasic acid, which also acts as an ether, was first known as paramalic acid, as it is metameric with malic acid. Heintz was the first to obtain it, together with glycollic acid, by heating chloracetic acid with caustic soda,[4] and Wurtz afterwards showed that it is obtained by oxidizing diethylene glycol.[5] The same substance is formed in large quantity when chloracetic acid is heated with the hydroxides of the alkaline earths, whilst caustic alkalis and other metallic hydroxides chiefly yield glycollic acid.[6] In order to prepare it in this way, monochloracetic acid is boiled with an excess of milk of lime, and the filtrate treated with carbon dioxide and concentrated somewhat; on addition of alcohol the calcium salts of glycollic and diglycollic acids separate out, and these may be readily separated by recrystallization, calcium diglycollate being less soluble in water than the glycollate. In order to prepare the free acid, the calcium salt is converted into the insoluble lead

[1] *Ann. Chem. Pharm.* lxxxix. 339.
[2] Kekulé, *ib.* cv. 286; Tscherniak and Norton, *Bull. Soc. Chim.* [2], xxx. 102.
[3] Naumann, *Ann. Chem. Pharm.* cxxix. 275.
[4] *Pogg. Ann.* cix. 470; cxv. 280.
[5] *Comptes Rendus*, li. 162; *Ann. Chem. Pharm.* cxvii. 136.
[6] Schreiber, *Journ. Prakt. Chem.* [2], xiii. 436; Heintz, *Ann. Chem. Pharm.* cxliv. 91.

salt, and this decomposed by sulphuretted hydrogen.[1] It crystallizes from water, in which it is easily soluble, in large transparent rhombic prisms containing one molecule of water, which is driven off completely at 100°. The anhydrous acid boils at 148°, and solidifies again to a crystalline mass on cooling. On heating with hydriodic acid, it is decomposed into acetic and glycollic acids, which latter, when an excess of hydriodic acid is present, is reduced to acetic acid.

Diglycollic acid forms both acid and normal salts. Those of the alkali metals are soluble; those of the other metals dissolve only with difficulty.

*Calcium Diglycollate*, $C_4H_4O_5Ca$, is scarcely soluble in cold and only slightly soluble in hot water. On cooling the solution it crystallizes in long glistening needles, which contain 6 molecules of water. On allowing the solution to evaporate slowly, a salt crystallizes out containing 3 molecules of water, and it can also be obtained with 1, 4, or 5 molecules of water.[2]

## SULPHUR COMPOUNDS OF GLYCOLYL.

507 *Thioglycollic Acid*, or *Mercapto-acetic Acid*, $CH_2(SH)CO_2H$, is obtained by the addition of chloracetic acid to an aqueous solution of potassium hydrosulphide. The potassium salt, separated from potassium chloride by crystallization and treatment with alcohol, is decomposed by sulphuric acid, and the acid extracted with ether. It is an oily colourless liquid, soluble in water, and having but little smell. As an acid and a mercaptan it can form three series of salts,[3] as well as different compound ethers.[4] *Thiodiglycollic Acid*, $S(CH_2.CO_2H)_2$, and *Dithioglycollic Acid*, $S_2(CH_2.CO_2H)_2$, have also been prepared.[5]

508 *Thetine Compounds.* These bodies, which correspond to the sulphine compounds (Part I. pp. 158 and 384), have been investigated by Crum-Brown and Letts.[6] Their bromides are formed by heating bromacetic acid with the sulphides of the alcohol radicals:

[1] *Ann. Chem. Pharm.* cxliv. 91.
[2] Mohs, *Zeitsch. Chem.* 1866, 495.
[3] Claesson, *Ann. Chem. Pharm.* clxxxvii. 113.
[4] Erlenmeyer and Lisenko, *Zeitsch. Chem.* 1862, 134; Claesson, *Ber. Deutsch. Chem. Ges.* viii. 120.
[5] Schulze, *Zeitsch. Chem.* 1865, 73; Schreiber, *Journ. Prakt. Chem.* [2], xiii. 472; Andreasch, *Ber. Deutsch. Chem. Ges.* xii. 1390; Claesson, *ib.* xiv. 409.
[6] *Edin. Phil. Trans.* xxviii. [2], 571.

$$\begin{array}{l} CH_2Br \\ | \\ CO_2H \end{array} + S(CH_3)_2 = \begin{array}{l} CH_2S(CH_3)_2Br \\ | \\ CO_2H. \end{array}$$

Dimethyl Thetine Bromide.

The compounds thus obtained are easily soluble in water, and crystallize from alcohol in large transparent rectangular tables.

*Dimethyl Thetine,* $\begin{array}{ccc} & CH_2 & \\ / & & \backslash \\ CO & & S(CH_3)_2 \\ \backslash & & / \\ & O & \end{array} + H_2O$, is obtained by acting with moist silver oxide on a solution of the bromide. It forms large deliquescent crystals, which are less soluble in alcohol than in water. It possesses a burning saline taste, and unites with acids, but not with weak ones such as carbonic or hydrocyanic, and this is easily understood as the substance is itself a salt. If it be allowed to stand for a week over sulphuric acid in a vacuum, it loses its water and becomes opaque.

The bromide has an acid reaction like all thetine salts. Its warm solution dissolves oxide of lead, and on cooling, laminæ of a double salt separate out, whilst dimethyl thetine remains in solution:

$$4\begin{array}{l} CH_2S(CH_3)_2Br \\ | \\ CO.OH \end{array} + 2Pb(OH)_2 = \begin{array}{l} CH_2S(CH_3)_2Br \\ | \\ CO.OPbBr \end{array} + PbBr_2 +$$

$$3\begin{array}{ccc} & CH_2 & \\ / & & \backslash \\ CO & & S(CH_3)_2 \\ \backslash & & / \\ & O & \end{array} + 4H_2O.$$

The other dimethyl thetine compounds are obtained from the bromide by decomposing it with soluble silver salts, and the same compounds are obtained by the action of acids upon dimethyl thetine.

The chloride, which is crystalline but very deliquescent, combines with platinum chloride to form the salt $(C_4H_9SO_2)_2PtCl_6+2H_2O$, a body crystallizing from hot water in orange-needles.

The ethyl ether, $Br(CH_3)_2SCH_2CO.OC_2H_5$, is formed by the union of ethyl bromacetate with methyl sulphide. It crystallizes in pearly glistening hygroscopic laminæ.

Letts has prepared several other thetine compounds with other

alcohol radicals, and these are less easily formed than dimethyl thetine, and with the greater difficulty the more carbon the radical contains, whilst the power of crystallization diminishes in the same ratio.[1]

509 *Sulpho-acetic Acid*, $CH_2(SO_3H)CO_2H$, was discovered by Melsens in 1842, who gave it the above name. He obtained it by the action of sulphur trioxide and fuming sulphuric acid on acetic acid.[2] It is also formed by treating acetamide or aceto-nitril with the fuming acid,[3] or by heating acetic acid with chlorsulphonic acid.[4] Its sodium salt is easily obtained by boiling chloracetic acid with a solution of normal sodium sulphite.[5] The sulphur compounds already described also yield this acid on oxidation with dilute nitric acid.[6] It remains behind as a syrup, on evaporation of the solution in a vacuum. This gradually solidifies to a needle-shaped mass which is very deliquescent. Sulphone-acetic acid is a strong dibasic acid, of which, however, only the normal salts have as yet been prepared.

510 *Thiocyanacetic Acid*, or *Rhodacetic Acid*, $CH_2(S.CN)CO_2H$. The ethyl ether of this body was obtained by Heintz, by acting with potassium thiocyanate on ethyl chloracetate.[7] On heating this with strong hydrochloric acid, he believed that he had obtained the free acid, but Claesson has shown that the substance which is then liberated is its isomeride, thiocarbimidacetic acid (p. 91). In order to prepare thiocyanacetic acid, powdered potassium thiocyanate is added to a concentrated solution of sodium chloracetate. The crystalline magma which is formed is then treated with boiling alcohol, when potassium chloride remains behind, and crystals of sodium thiocyanacetate are deposited from the filtrate. The well-cooled aqueous solution of this salt is then decomposed by sulphuric acid and at once extracted with ether.[8]

Rhodacetic acid is a colourless and odourless oil which, when gently warmed, changes into a porcelain-like mass difficultly soluble in water, and crystallizing from this solution in groups of stellar needles. It forms with the metals of the alkalis and

[1] *Edin. Phil. Trans.* xxviii. [2], 583.
[2] *Ann. Chem. Pharm.* xliv. 97 ; lii. 275.
[3] Buckton and Hofmann, *Proc. Roy. Soc.* viii. 158 ; *Ann. Chem. Pharm.* c. 141.
[4] Baumstark, *ib.* cxl. 75.
[5] Collmann, *ib.* cxlviii. 101.
[6] Carnis, *ib.* cxxiv. 52.
[7] *Ib.* cxxxvi. 223.
[8] Claesson, *Ber. Deutsch. Chem. Ges.* x. 1346.

the alkaline earths crystallizable salts, whereas those of the other metals are readily decomposed with formation of the thioglycollates. When sulphate of copper is brought into a solution of rhodacetic acid, a black amorphous precipitate is formed after some time, consisting of cuprous thioglycollate, $(CH_2)_2S_2Cu_2(CO_2)_2Cu_2$. This reaction is very characteristic (Claesson).

*Thiocarbimidacetic Acid,* or *Mustard-oil-acetic Acid,* $CH_2(N.CS)CO_2H$, was obtained by Volhard by boiling glycolyl thio-urea (p. 97) with hydrochloric acid:

$$\begin{matrix} CH_2.NH \\ | \\ CO.NH \end{matrix}\!\!\diagdown\!\!\diagup CS + HCl + H_2O = \begin{matrix} CH_2.N.CS \\ | \\ CO.OH \end{matrix} + NH_4Cl.$$

It is soluble in hot water, difficultly soluble in cold, and crystallizes in rhombic tables, melting at 125°—126°. As an amido-compound it acts as a weak acid, the salts being many of them partially decomposed by water.[1]

*Nitroacetic Acid,* $CH_2(NO_2)CO_2H$. This body is not known in the free state. When attempts are made to form the potassium salt by heating a solution of potassium chloracetate with potassium nitrite, carbon dioxide and nitromethane (Part I. p. 227) are obtained.

The ethyl ether is however known, and this is obtained by the action of ethyl bromacetate on silver nitrite. This liquid boils, not without decomposition, at 151°—152°, and on treatment with tin and hydrochloric acid is converted into amido-acetic acid.[2]

## AMIDO-COMPOUNDS OF GLYCOLYL.

511 Many of these compounds are of great physiological interest, inasmuch as they and several of their derivatives occur both in the animal and in the vegetable kingdoms, as the products of decomposition of higher and more complicated compounds. In addition to those now described, others exist which will be noticed in the further course of this work.

*Glycolamide,* $CH_2(OH).CO(NH_2)$, is obtained by the action of ammonia on ethyl glycollate or glycolide. It forms colourless

[1] *Journ. Prakt. Chem.* [2], ix. 6.
[2] Forcrand, *Bull. Soc. Chim.* xxxi. 536.

crystals which fuse at 120°. Aqueous hydrochloric acid converts it into glycolic acid and sal-ammoniac.

*Amido-acetic Acid*, or *Glycocoll*, $CH_2(NH_2)CO_2H$, was first prepared by Braconnot in 1820, being contained amongst the products of the action of sulphuric acid on glue, and received from him the name of *Sucre de gélatine*, on account of its sweet taste.[1] Dessaignes found later on that the same body occurs as a product of decomposition of hippuric acid.[2] This latter chemist as well as Laurent,[3] Mulder,[4] and Horsford [5] determined its composition, and the last-named chemist gave to it the name of glycocoll, by which it is usually known (γλυκύς, sweet; κόλλα, glue). Strecker then found that it is a decomposition product of glycocholic acid, one of the constituents of bile,[6] and since that it has been obtained from various other complicated carbon compounds. According to Chittenden it is found in the muscle of the edible *Pecten irradians*.[7]

Amido-acetic acid was first artificially obtained by Perkin and Duppa, by acting with ammonia on bromacetic acid.[8] Cahours then showed that chloracetic acid may also be used for this purpose.[9] Its formation from cyanogen is peculiar.[10] If this gas be led into a boiling solution of concentrated hydriodic acid, the following reaction takes place:

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 5HI + 2H_2O = \begin{matrix} CH_2.NH_2 \\ | \\ CO.OH \end{matrix} + NH_4I + 2I_2.$$

The method proposed by Braconnot was formerly employed for the preparation of glycocoll. According to Mulder a better yield is obtained when the glue is boiled with hot caustic potash instead of sulphuric acid.[11] It is most conveniently prepared from hippuric acid (benzoyl-amido-acetic acid), a body occurring in the urine of graminivorous animals. This substance, when warmed with four times its weight of fuming hydrochloric acid, undergoes the following change:

$$\begin{matrix} CH_2NH(C_6H_5.CO) \\ | \\ CO_2H \end{matrix} + H_2O = \begin{matrix} CH_2.NH_2 \\ | \\ CO_2H \end{matrix} + C_6H_5CO_2H.$$

[1] *Ann. Chim. Phys.* [2], xiii. 114.
[2] Dessaignes, *Ann. Chem. Pharm.* lviii. 322.
[3] *Compt. Rend.* xxii. 789.
[4] *Journ. Prakt. Chem.* xxxviii. 294.
[5] *Ann. Chem. Pharm.* lx. 1.
[6] *Ib.* lxv. 130; lxvii. 16.
[7] *Ib.* clxxviii. 266.
[8] *Quart. Journ. Chem. Soc.* xi. 22.
[9] *Compt. Rend.* xlvi. 1044; cvii. 147.
[10] Emmerling, *Ber. Deutsch. Chem. Ges.* vi. 1352.
[11] *Journ. Prakt. Chem.* xvi. 290.

The solution is then diluted with water and allowed to cool, when a large portion of the benzoic acid which is formed crystallizes out. The filtrate is evaporated almost to dryness and then boiled with water for some time, in order to drive off the remaining benzoic acid. In this way glycocoll hydrochloride is obtained, and this is decomposed with oxide of lead or silver oxide.

The preparation of amido-acetic acid from chloracetic acid or bromacetic acid is not economical, because large quantities of diglycolamidic acid, $NH(CH_2.CO_2H)_2$, and triglycolamidic acid, $N(CH_2.CO_2H)_3$, are produced.[1]

Glycocoll dissolves in 4·3 parts of cold, and more readily in hot water. It is insoluble in absolute alcohol and spirit of wine. It crystallizes in large hard monoclinic tables which grate between the teeth, have a sweet taste and fuse at 170°, undergoing decomposition with separation of carbon when heated to a higher temperature. Its solution is coloured deep red by ferric chloride and deep blue by copper salts.

As an amido-acid glycocoll is at once a base and an acid, or rather, as it has a neutral reaction, a salt (p. 18). Of its numerous compounds, only the more important can here be mentioned.

512 *Metallic Compounds of Glycocoll.* Amongst these the copper salt is very characteristic. It is obtained by boiling a glycocoll solution with copper oxide. On cooling or addition of alcohol, the compound, having the formula $(C_2H_4NO_2)_2\ Cu + H_2O$, crystallizes in fine blue needles. These dissolve in caustic potash, yielding a deep blue solution. If glycocoll and caustic potash be added to a solution of copper sulphate the solution also becomes dark blue, and the above salt is separated on addition of alcohol. The silver salt, $C_2H_4NO_2Ag$, difficultly soluble in water, is deposited in granular crystals.

*Acid Compounds of Glycocoll.* Of these, two series are known (p. 18), and all crystallize well.

*Saline Compounds of Glycocoll.* It has already been stated that glycocoll combines with many salts, and these compounds are also readily obtained crystalline.

*Ethyl Amido-acetate*, $CH_2(NH_2)CO_2.C_2H_5$. When glycocoll is heated with ethyl iodide and alcohol, the compound, $CH_2(NH_3I)CO_2.C_2H_5$, is formed, crystallizing in rhombic prisms. When its aqueous solution is heated with silver chloride, the corresponding chloride is formed. This crystallizes in fine needles and

[1] Heintz, *Ann. Chem. Pharm.* cxxii. 257; cxxxvi. 213.

when treated with water and silver oxide yields the ethyl ether, which is deposited in small crystals, and in aqueous solution easily decomposes into glycocoll and alcohol.

*Amido-Glycolamide,* $CH_2(NH_2)CO(NH_2)$. This is formed together with the above-named compound by the action of a large excess of alcoholic ammonia on ethyl chloracetate, and it is formed, though in less quantity, in a similar way from glycocoll. On evaporating the solution a syrup remains which gradually crystallizes. Boiling water decomposes it into glycocoll and ammonia.

513 *Methyl-glycocoll,* or *Sarcosine,* $\begin{array}{ccc} & CH_2 & \\ \diagup & & \diagdown \\ CO & & N(CH_3)H_2 \\ \diagdown & & \diagup \\ & O & \end{array}$. This body, which was first believed to be an alkaloid, was obtained by Liebig in 1847 as a product of the decomposition of creatine (p. 98), a body occurring in the muscular tissue.[1] Volhard then showed that this compound is formed when ethyl chloracetate is heated with aqueous methylamine.[2] It is very soluble in water, has a sharp but sweet taste, and crystallizes in transparent rhombic prisms. In its chemical relations it closely resembles glycocoll. Its platinum salt is especially characteristic. This is soluble in water, and crystallizes readily in large honey-yellow octohedrons.[3]

By the action of ethylamine on chloracetic acid, ethyl-glycocoll is formed, whilst diethylamine yields diethyl-glycocoll.[4] Both deposit in deliquescent crystals.

The following compounds are metameric with ethyl glycocoll and ethyl amido-acetate.

*Ethyl Glycolamide,* $CH_2(OC_2H_5)CO.NH_2$, is formed by the action of ammonia on the ethyl ether of ethyl glycollic acid,[5] and crystallizes from water in large prisms having a cooling taste. These melt below 100°, the liquid boiling at 225°, and on heating with phosphorus pentoxide, the nitril, $CH_2(OC_2H_5)CN$, is formed, an aromatic smelling liquid boiling at 134°—135°.[6]

*Glycol-ethylamide,* $CH_2(OH)CO.NH(C_2H_5)$, is formed by acting with ethylamine on ethyl glycollate. It is a thick liquid soluble in water, boiling at about 250° (Heintz).

[1] *Ann. Chem. Pharm.* lxii. 310.
[2] *Ib.* cxxiii. 261.
[3] Heintz, *ib.* cxxix. 33.
[4] Heintz, *ib.* cxl. 218.
[5] Heintz, *ib.* cxxix. 27.
[6] Henry, *Ber. Deutsch. Chem. Ges.* vi. 259; Tscherniak and Norton, *ib.* xii. 369.

514 *Trimethyl-glycocoll*, or *Betaïne*, $CO\begin{<}CH_2\\O\end{>}N(CH_3)_3$. This weak base was first obtained by Liebreich by careful oxidation of choline.[1] He then artificially prepared it by acting upon trimethylamine with chloracetic acid,[2] and termed it oxyneurine. Before this Scheibler had noticed a base which occurs in the juice of the sugar-beet (*Beta vulgaris*), which he afterwards investigated, and to which he gave the name of *Betaïne*.[3] The identity of this substance with oxyneurine was proved both by himself and by Liebreich.[4]

Trimethyl-glycocoll is found in *Lycium barbarum*, and the body got from this was formerly believed to be a peculiar alkaloid, described under the name of *Lycine*. Its identity with betaïne was shown by Husemann.[5]

In order to prepare betaïne a slight excess of lead acetate is added to the beet or the molasses diluted with water, the precipitate filtered off and this decomposed by dilute sulphuric acid. The acid solution gives with phosphotungstic acid a precipitate which is then decomposed with milk of lime.[6]

Betaïne crystallizes from alcohol in large glistening deliquescent crystals containing one molecule of water, which is evolved at 100°. In its chemical relations it resembles glycocoll. The chloride, $C_5H_{12}NO_2Cl$, forms large stable monoclinic crystals. It combines with platinum chloride to form the compound $(C_5H_{12}NO_2)_2PtCl_6 + 2H_2O$, a body deposited in large yellow crystals which effloresce on exposure.

*Muscarine*, $CH(OH)_2CH_2N(CH_3)_3OH$, is found together with choline in a toadstool, fly agaric (*Agaricus muscarius*),[7] and is formed by the oxidation of the latter base with strong nitric acid.[8] The free base has a strongly alkaline reaction and crystallizes in thin deliquescent laminæ. The hydrochloride is also very deliquescent, and forms the platinichloride $(C_5H_{14}NO_2)_2PtCl_6 + 2H_2O$, which is difficultly soluble in water. Muscarine is the poisonous constituent of the toadstool.

[1] *Ber. Deutsch. Chem. Ges.* ii. 13.
[2] *Ib.* ii. 167.
[3] *Ib.* ii. 292.
[4] *Ib.* iii. 155 and 161.
[5] *Arch. Pharm.* [3], vi. 216 ; *Jahresb.* 1875, 828.
[6] See Frühling and Schulz, *Ber. Deutsch. Chem. Ges.* x. 1070.
[7] Schmiedeberg and Koppe, *Jahresb.* 1870, 875.
[8] Schmiedeberg and Harnack, *ib.* 1876, 804.

## CARBAMIDE COMPOUNDS OF GLYCOLYL.

515 *Glycolyl-urea*, $CO\begin{<}{NH—CH_2}{NH—CO}$, was first obtained by Baeyer as a product of decomposition of uric acid and allantoïn, and termed by him *Hydrantoïn*. He also obtained this compound artificially by heating alcoholic ammonia with bromacetyl urea, a body prepared by acting on urea with bromacetyl bromide:[1]

$$CO\begin{<}{NH_2}{NH.CO.CH_2Br} + NH_3 = CO\begin{<}{NH.CH_2}{NH.CO} + NH_4Br.$$

Glycolyl-urea is easily soluble, especially in hot water, depositing in large but not well-formed crystals. These have a slight sweet taste, and melt at 206°.

*Glycoluric Acid*, or *Hydrantoïc Acid*, $(NH_2)CO.NH.CH_2.CO_2H$. The barium salt of this acid is obtained from the foregoing compound by boiling it with baryta-water. This, when decomposed with dilute sulphuric acid, yields glycoluric acid, a body crystallising from hot water in monoclinic prisms.[2] It is also formed when an aqueous solution of glycocoll sulphate is evaporated with potassium cyanate,[3] or when glycocoll and urea are boiled for some time with baryta-water.[4]

*Methyl-hydrantoïn*, $CO\begin{<}{N(CH_3)—CH_2}{NH——CO}$, was first obtained as a product of decomposition of creatinine (p. 99), and is also formed when sarcosine is fused with urea.[5] It forms clear crystals which have a faint acid reaction and melt at 145°.

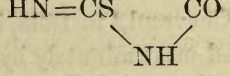
*Methyl-hydrantoïc Acid*, $(NH_2)CO(NCH_3)CH_2.CO_2H$. If, in addition to its usual food, such a quantity of sarcosine be given to a dog that the amount of nitrogen which it contains be exactly equal to that which the dog excretes daily, uric acid and urea completely disappear, and in their place methyl-hydrantoïc acid and other nitrogenous compounds make their appearance.[6]

[1] *Ann. Chem. Pharm.* cxxx. 158; *Ber. Deutsch. Chem. Ges.* viii. 614.
[2] Herzog, *Ann. Chem. Pharm.* cxxxvi. 278.
[3] Wislicenus, *ib.* clxv. 103.
[4] Baumann and Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* vii. 34.
[5] Huppert, *ib.* vi. 1278. [6] Schultzen, *ib.* v. 578.

The same acid is formed when sarcosine, potassium cyanate, and ammonium sulphate are allowed to stand together in aqueous solution, or when a mixture of sarcosine and urea is boiled with baryta-water.[1] It crystallizes from alcohol in transparent needles. When heated alone it is converted easily into methyl-hydrantoïn, and when heated with baryta-water under pressure it decomposes with formation of carbon dioxide, ammonia, and sarcosine.

*Glycolyl Thio-urea*, or *Sulphohydrantoïn*, $CS\begin{cases} NH—CH_2 \\ \quad\quad | \\ NH—CO \end{cases}$. The chloride of this body is obtained by heating thiocarbamide with chloracetic acid. It crystallizes in fine prisms, and yields, on treatment with alkalis, the thio-urea which crystallizes from hot water in long glistening needles.[2] When boiled with baryta-water, barium thioglycollate together with dicyandiamide is produced.[3] According to Liebermann and Lange it appears probable, from this decomposition as well as for other reasons, that the constitution of sulphohydrantoïn and of mustard-oil acetic acid (p. 91) is represented by the following formulæ:[4]

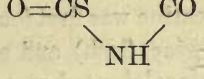
Glycolyl Thio-urea.



$$HN{=}CS\begin{cases} CH_2 \\ \quad\quad | \\ NH \end{cases}CO$$

Mustard-oil Acetic Acid.

$$O{=}CS\begin{cases} CH_2 \\ \quad\quad | \\ NH \end{cases}CO$$



The formation of the latter compound from thiocyanacetic acid is in this case easily understood.

## GUANIDINE COMPOUNDS OF GLYCOLYL.

516 *Glycocyamine*, or *Guanidoacetic Acid*, $C_3H_7N_3O_2$, was obtained by Strecker by heating together for some days aqueous solutions of glycocoll and cyanamide, to which some ammonia had been added.[5] It is also formed when glycocoll is heated with guanidine carbonate.[6] It is deposited in small crystals which are

[1] Baumann and Hoppe-Seyler, *loc. cit.*
[2] Volhard, *Ann. Chem. Pharm.* clxvi. 383.
[3] Andreasch, *Ber. Deutsch. Chem. Ges.* xii. 1385.
[4] *Ib.* xii. 1588.
[5] *Compt. Rend* lii. 1212; *Jahresb.* 1861, 530.
[6] Nencki and Sieber, *Journ. Prakt. Chem.* [2], xvii. 477.

difficultly soluble in cold and more easily in boiling water and insoluble in alcohol. It acts at once as a weak base and as an acid,[1] and hence in the free state it may be considered to be a salt:

$$\begin{array}{l} CH_2.NH.C=NH \\ | \quad\quad | \\ CO.OH \quad NH_2 \end{array} = \begin{array}{l} CH_2.NH.C=NH \\ | \quad\quad | \\ CO—O—NH_3. \end{array}$$

*Glycocyamidine*, or *Gycolyl Guanidine*, $C_3H_5N_3O$, is formed when glycocyamine hydrochloride is heated to 160°. Its constitution is, therefore, represented by the following formula:

$$\begin{array}{l} CH_2.NH \\ | \quad\quad C=NH. \\ CO.NH \end{array}$$

The free base is obtained from this hydrochloride by boiling it with lead hydroxide. It crystallizes in small laminæ, easily soluble in water, and having an alkaline reaction. The hydrochloric acid compound is also very soluble, and forms a platinichloride, $(C_3H_6N_3O)_2PtCl_6$, crystallizing in yellow needles. The zinc double salt, $(C_3H_6N_3O)_2ZnCl_2$, is a characteristic one, being difficultly soluble, and also crystallizing in needles.

### Creatine, or Methyl Guanidoacetic Acid, $C_4H_9N_3O_2$.

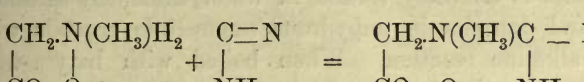
517 Creatine was first found by Chevreul,[2] in 1835, in the juice of flesh (κρέας, flesh), and examined most minutely by Liebig, in 1847, in his celebrated research on the constituents of the liquids of flesh.[3] It is found in the flesh of all vertebrates and also in small quantity in the brain and blood. The flesh of game and of poultry is best suited for its preparation, as this appears to contain about 0·35 per cent. The flesh is finely cut up, freed from fat as much as possible, well kneaded several times with its own weight of water, and the liquid well pressed out in a coarse linen bag. The liquid is then heated to boiling to separate the albumen, &c., and filtered. The phosphoric acid which is present is next separated by the addition of baryta-water and the filtrate evaporated to one-twentieth its bulk. The creatine crystallizes out on standing, a small quantity of creatinine present being removed by washing with alcohol.

As the extract of meat is prepared now on the manufacturing

[1] Engel, *Bull. Soc. Chim.* [2], xxiv. 274.
[2] *Ann. Chem. Pharm.* iv. 293.
[3] *Ib.* lxii. 257.

scale, this may conveniently be employed for preparing creatine. It is dissolved in 20 parts of water and acetate of lead added so long as a precipitate forms, the filtrate treated with sulphuretted hydrogen and the solution operated upon as above described.[1]

Creatine has been artificially prepared by Volhard by heating an alcoholic solution of sarcosine with freshly prepared cyanamide for some hours to 100°.[2]



Creatine dissolves in 75 parts of cold water and more readily in hot water, crystallizing in bright glistening transparent monoclinic prisms which contain one molecule of water. When heated to 100° they become opaque from loss of water. It has a faintly bitter taste and is not soluble in absolute alcohol or ether. When boiled with baryta-water it decomposes into sarcosine and urea, and when its aqueous solution is heated with mercuric oxide, oxalic acid and methyl-guanidine are formed.

Creatine has a neutral reaction, but combines with acids as well as with a variety of salts, in this respect resembling glycocoll. The compounds thus obtained usually crystallize well.

## Creatinine, or Methyl Glycolyl Guanidine, $C_4H_7N_3O$.

518 This body was first obtained by Liebig, who heated creatine in a current of hydrochloric acid to 100°, when the hydrochloride of a "true organic alkaloid" is formed. Creatinine sulphate is easily formed when creatine is evaporated to dryness with the calculated quantity of dilute sulphuric acid. By decomposing this with baryta-water, or by boiling the hydrochloride with an excess of oxide of lead in order to form an insoluble basic lead chloride, a solution of the free base is obtained.

Creatinine occurs in nature in human urine and in that of various animals, and from the first source it can be readily obtained (Liebig). The liquid is neutralized with milk of lime, chloride of calcium added in order to precipitate the phosphates, and the whole evaporated until salts begin to crystallize out. A concentrated solution of zinc chloride is then added to the

[1] Mulder and Mouthaan, *Zeitsch. Chem.* 1869, 341. [2] *Jahresb.* 1868, 685.

mother-liquor, when the zinc chloride compound already described slowly separates out and is decomposed on boiling with water and an excess of lead hydroxide.[1]

It is perhaps simpler to make use of mercuric chloride, which also forms an insoluble compound with creatinine, which is easily decomposed by sulphuretted hydrogen. Instead of human urine that of the horse may be employed.[2]

Creatinine is tolerably soluble in water, difficultly soluble in alcohol, and deposits in anhydrous monoclinic crystals which have an alkaline reaction. When boiled with baryta-water, ammonia and methyl hydrantoïn (p. 96) are formed:

$$\begin{array}{l} CH_2.N.CH_3 \\ | \quad \diagdown C = NH \\ CO.NH \end{array} + H_2O = \begin{array}{l} CH_2.N.CH_3 \\ | \quad \diagdown CO \\ CO.NH \end{array} + NH_3.$$

Creatinine in aqueous solution readily undergoes change, passing into creatine. This takes place more quickly if ammonia, lead oxide, or other bases be present.

*Salts of Creatinine.* Creatinine is a strong base decomposing ammonium salts. The hydrochloride, $C_4H_8N_3OCl$, crystallizes from hot alcohol in short transparent prisms, and from water, in which it is very soluble in transparent scales. The platinichloride, $(C_4H_8N_3O)_2PtCl_6$, forms yellowish-red granular crystals, or orange-red prisms. The sulphate, $(C_4H_8N_3O)_2SO_4$, crystallizes from hot alcohol in transparent quadratic tables.

*Creatinine Zinc Chloride,* $(C_4H_7N_3O)_2ZnCl_2$, forms oblique rhombic prisms or small needles that form warty concretions. It is difficultly soluble in water and almost insoluble in strong alcohol. It forms with hydrochloric acid an easily soluble compound, $(C_4H_8N_3OCl)_2ZnCl_2$, which crystallizes well.

Creatinine also forms well crystallized compounds with other salts. These have been especially studied by Neubauer.

Creatinine forms with ethyl iodide the compound, $C_4H_7N_3O(C_2H_5)I$, crystallizing in long glistening needles, and this is converted by the action of moist silver oxide into the corresponding strongly alkaline hydroxide.[3]

[1] Neubauer, *Ann. Chem. Pharm.* cxix. 37.
[2] Maly, *ib.* clix. 279.
[3] Neubauer, *ib.* cxx. 257.

### Phosphorus Compounds of Glycolyl.

519 *Phosphortrimethyl Glycocoll*, or *Phosphor-Betaïne*, $CO\begin{matrix}\diagup CH_2 \diagdown \\ \diagdown O \diagup\end{matrix}P(CH_3)_3$. The hydrochloride, $CO_2.CH_2.P(CH_3)_3HCl$, of this body is formed by the action of trimethyl phosphine on monochloracetic acid. It is very deliquescent, as is the base obtained from it by means of silver oxide. The platinichloride separates out from hot water in large orange-red rhombic crystals.[1]

*Phosphor-Ethyl-Betaïne*, $CO\begin{matrix}\diagup CH_2 \diagdown \\ \diagdown O \diagup\end{matrix}P(C_2H_5)_3$, was first prepared by Hofmann by the action of triethyl phosphine on chloracetic acid,[2] and afterwards exactly investigated by Letts.[3] It is also very deliquescent, and contains water of crystallization, which it gives off slowly in a vacuum over sulphuric acid. If the aqueous base be heated, it is transformed into the isomeric acid-carbonate of methyl-triethyl phosphonium, $CO\begin{cases}OH \\ OP(C_2H_5)_3CH_3.\end{cases}$

The nitrate crystallizes in needles, has an acid reaction, and is not deliquescent; the platinichloride forms large crystals tolerably soluble in hot water. The salts decompose on heating into carbon dioxide, and the salts of methyl-triethyl-phosphonium, and in this respect they resemble the thetine salts, and not those of betaïne, which either sublime or are decomposed into trimethylamine and substituted acetic acid.

## THE OXALYL COMPOUNDS.

### The Aldehydes of Oxalic Acid.

520 Oxalic acid, being a dibasic acid, forms two aldehydes:

| (1) Glyoxal. | (2) Glyoxylic Acid. |
|---|---|
| COH | COH |
| \| | \| |
| COH. | CO.OH. |

[1] A. H. Meyer, *Ber. Deutsch. Chem. Ges.* iv. 734.
[2] *Proc. Roy. Soc.* xi. 530.
[3] *Ib.* Edin. 1880-1881, 40; and Neubauer, *Ann. Chem. Pharm.* cxix. 37; cxx. 257.

These bodies, discovered by Debus, are formed together with oxalic and glycollic acids when alcohol and various other compounds, such as glycol, aldehyde, &c., are oxidized with nitric acid.[1]

*Glyoxal*, or *Oxalaldehyde*, $C_2H_2O_2$. According to Lübawin the following is the best mode of preparing this body. Into a glass cylinder, having a capacity of 250 cc., are poured in separate layers, by means of a tube-funnel which reaches to the bottom, first 64 cc. of nitric acid, of specific gravity 1·37, which has been mixed with 2·5 cc. of the fuming acid, then 20 cc. of water, and lastly 60 cc. of aqueous aldehyde of 50 per cent. The whole is allowed to remain at the temperature of the air for four to five days, and then the liquid evaporated on a water-bath, when almost perfectly pure glyoxal remains. In order to purify it further, it is shaken with a concentrated solution of hydrogen sodium sulphite, when a compound, having the composition $\begin{matrix}CH(OH)SO_3Na\\|\\CH(OH)SO_3Na,\end{matrix}$ is formed, depositing in small hard crystals, which may be purified by crystallization from solution in water. By double decomposition with barium chloride, the corresponding barium salt is obtained. This is but difficultly soluble in water, and yields, on decomposition with dilute sulphuric acid, a solution of glyoxal, this compound remaining on evaporation as an amorphous deliquescent mass. Glyoxal possesses the characteristic properties of an aldehyde, and reduces ammoniacal silver. By the action of lime or baryta it is easily converted into glycollic acid:

$$COH.COH + H_2O = CH_2(OH).CO.OH.$$

Hence both oxidation and reduction occurs. The aldehydes of the monobasic acid exhibit a similar reaction, but in this case one molecule of alcohol and one of monobasic acid are produced. If an acetic acid solution of glyoxal be saturated with hydrochloric acid, hexglyoxal hydrate, $C_{12}H_{14}O_{13}$, or $C_{12}H_{12}O_{12} + H_2O$, is formed. This is an amorphous powder resembling starch, dissolving in strong acids or boiling alcohol.[2]

If glyoxal be warmed with aqueous ammonia to from 60° to 70°, the following two singular basic compounds are formed (Debus):

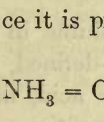
[1] Debus, *Ann. Chem. Pharm.* c. 5; cii. 20; cvii. 199; cx. 319; cxviii. 253; chiff, *ib.* clxxii. 1; Lübawin, *Ber. Deutsch. Chem. Ges.* viii. 768; x. 1366.

[2] H. Schiff, *Ann. Chem. Pharm.* clxxii. 1.

521 *Glyoxalin*, $C_3H_3N(NH)$, is the chief product; it is a body easily soluble in water, and crystallizes in fine prisms, possessing a faint fish-like smell; it fuses at 88°—89°, and boils at 266°, and its vapour density is 2·35.[1] With acids it forms neutral crystallizable salts. It contains one atom of hydrogen capable of replacement by silver as well as by alcohol radicals. It is not oxidized by a solution of chromic acid, and reducing agents are also without action upon it. Bromine converts it into *tribromoxalin*, $C_3Br_3N(NH)$, crystallizing from alcohol in silky needles, possessing a distinctly acid character, and remarkable as being, with the exception of hydrocyanic acid, the only acid containing carbon which does not contain oxygen or sulphur. In the formation of glyoxalin, formic acid is produced, and hence it is produced according to the following reaction:

$$2C_2H_2O_2 + 2NH_3 = C_3H_4N_2 + CH_2O_2 + 2H_2O.$$

Its constitution is not positively known, but it is probably represented by the following formula:



*Glycosin*, $C_6H_6N_4$, is formed in smaller quantities than the preceding compound. It crystallizes in needles which on heating volatilize without melting; it is scarcely soluble in cold water, and is difficultly soluble in hot, and forms salts which crystallize well. Its constitution is probably similar to that of hexmethylenamine (p. 26), but with the difference that instead of the six diad methylene groups it contains three tetrad groups, $C_2H_2$.

522 *Glyoxylic Acid*, or *Glyoxalic Acid*, $CHO.CO_2H + H_2O$, or $CH(OH)_2.CO_2H$. Debus gave to this body the first of these formulæ, but the latter formula is, as Duppa and Perkin[2] have shown, the more probable, as the acid and all its salts (with the exception of the ammonium compound, which does not behave as a salt), must, according to the first formula, contain one molecule of water which cannot be removed without decomposing the compound. Glyoxylic acid has, accordingly, a constitution similar to that of chloral hydrate.

[1] Wyss, *Ber. Deutsch. Chem. Ges.* ix. 1543; x. 1365.
[2] *Journ. Chem. Soc.* xxi. 197.

In order to prepare glyoxylic acid it is best to start from dibromacetic acid, which is easily obtained by the action of bromine upon acetic anhydride. When its silver salt is boiled with water, equal molecules of glyoxylic acid and dibromacetic acid are formed:

$$2C_2HBr_2O_2Ag + 2H_2O = C_2H_4O_4 + C_2H_2Br_2O_2 + 2AgBr.$$

If the liquid be now neutralized with silver carbonate, and again boiled, the following reaction takes place:[1]

$$C_2H_3O_4Ag + C_2HBr_2O_2Ag + 2H_2O = 2C_2H_4O_4 + 2AgBr.$$

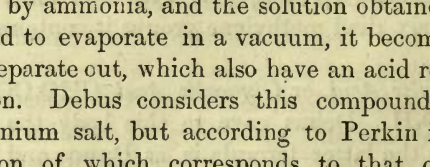
Böttinger has fully described the preparation of this acid from alcohol and nitric acid.[2]

Glyoxylic acid is very easily soluble in both water and alcohol, and crystallizes in small, ill-defined, probably monoclinic prisms, which taste like tartaric acid, melt on heating, but cannot be distilled without decomposition. This body possesses all the properties of an aldehyde. It forms crystalline compounds with the sulphites of the alkali metals, such as the sodium salt, $CH(OH)SO_3Na.CO_2Na$; it reduces ammoniacal silver solution, and when brought in contact with strong bases, it forms a mixture of oxalic acid and glycollic acid, whilst nascent hydrogen reduces it to glycollic acid.

*Potassium Glyoxylate*, $C_2H_3KO_4$, is an easily soluble crystalline powder, which begins to decompose at 100°.

*Calcium Glyoxylate*, $(C_2H_3O_4)_2Ca$, is difficultly soluble in cold water, and crystallizes in hard prisms.

When decomposed by ammonium oxalate, or when glyoxylic acid is neutralized by ammonia, and the solution obtained by either method allowed to evaporate in a vacuum, it becomes acid, and small prisms separate out, which also have an acid reaction after recrystallization. Debus considers this compound to be the normal ammonium salt, but according to Perkin it is an acid, the constitution of which corresponds to that of aldehyde-ammonia:




[1] Perkin, *Journ. Chem. Soc.* 1877, ii. 90.
[2] Liebig's *Ann.* cxcviii. 206.

*Silver Glyoxylate*, $C_2H_3AgO_4$, is a difficultly soluble crystalline powder, which soon blackens on exposure to light.

*Diethyl Glyoxylic Acid*, $CH(OC_2H_5)_2.CO_2H$. The sodium salt of this acid was obtained by Fischer and Geuther[1] by heating tetrachlorethylene with sodium ethylate, when ethyl-dichloracetate is formed as an intermediate product, so that the salt is most simply got by heating dichloracetic acid with an alcoholic solution of sodium ethylate.[2] When it is decomposed by dilute sulphuric acid, and the liquid shaken with ether, the acid is taken up, and on evaporating the ethereal solution, it remains behind as an oily liquid which, in contact with water, is easily converted into alcohol and glyoxylic acid.

The ethyl ether, $CH(OC_2H_5)_2CO_2(C_2H_5)$, is obtained by heating with ethyl iodide, and it is also formed when glyoxylic acid is heated with absolute alcohol (Perkin). It is a highly refracting liquid, possessing a fruity smell and burning taste, and boiling at 199°.

## OXALIC ACID, $C_2H_2O_4$.

523 This acid occurs as the hydrogen potassium salt in a variety of plants, such as the wood-sorrel, *Oxalis acetosella*, and in other species of oxalis and rumex. From the older names of these (acetosa, acetosella) it would appear that in former times they were believed to contain acetic acid.

At the beginning of the seventeenth century the salt obtained from the above plants was considered to be a kind of tartar, and its preparation was minutely described by Boerhave in his *Elementa Chemiæ*.[3] It was afterwards more completely investigated by F. P. Savary, whose *Dissertatio de sale acetosellæ* appeared in 1773, but still the nature of the acid which it contained remained a matter of doubt. Its special characteristics were first pointed out by Wiegleb in 1779, who discovered the fact that it has the power of rendering lime-water turbid.

In 1776 Scheele obtained an acid by acting with nitric acid upon sugar; and this was further investigated by Bergman, and described in his *Dissertatio de acido sacchari*, published in 1776. Amongst other remarks he there states that this acid cannot

[1] *Jenaer Zeitsch. Chem.* i. 54; Geuther and Brockhoff, *Journ. Prakt. Chem.* [2], vii. 102.

[2] Schreiber, *Zeits-h. Chem.* 1870, 167.

[3] Tomus secundus, p. 37.

only be obtained from a variety of bodies containing sugar, but also from meal, gum, and other vegetable matters, and that, on heating, a part of the acid sublimes, whilst another part yields a gas, half of which consists of fixed air, and the other of an air which burns with a blue flame.

The acid obtained from sugar, and that obtained from the various varieties of oxalis were usually supposed to be different substances, until Scheele in 1784 showed that they are identical.

Oxalic acid was first naturally considered to be an organic acid, but as it was found that many of its salts contained no hydrogen, this acid was for a long time classed as an inorganic compound, and looked upon as the hydrate of the hypothetical carbon sesquioxide, $C_2O_3$, which was termed anhydrous oxalic acid.

Various salts of oxalic acid occur in nature, and these will be mentioned in their proper place. In the free state it occurs in *Boletus igniarius*, and also, according to some observers, in the juice of the chick-pea.

Oxalic acid is obtained synthetically in a variety of ways.

(1) In the first place it occurs when the formate of an alkali-metal is gently heated:[1]

$$\begin{array}{c} H.CO.OK \\ H.CO.OK \end{array} = \begin{array}{c} H \\ | \\ H \end{array} + \begin{array}{c} CO.OK \\ | \\ CO.OK. \end{array}$$

(2) Its ammonium salt is formed, together with other products, when an aqueous solution of cyanogen is allowed to stand for some time:

$$\begin{array}{c} CN \\ | \\ CN \end{array} + 4H_2O = \begin{array}{c} CO.ONH_4 \\ | \\ CO.ONH_4. \end{array}$$

Hence cyanogen is the nitril of oxalic acid, or of *dicarboxyl* (dioxalyl).

(3) The formation of oxalic acid from carbon dioxide[2] is of special interest. If this gas be passed over sodium heated to 360°, and finely divided with sand, sodium oxalate is formed:

$$2CO_2 + Na_2 = C_2O_4Na_2.$$

The potassium salt may be obtained in the same way by

[1] Dumas and Stas, *Ann. Chem. Pharm.* xxxv. 137; Péligot, *Ann. Chim. Phys.* [2], lxxiii. 220; Erlenmeyer and Gütschow, *Chem. Centralb.* 1868, 420.

[2] Drechsel, *Ann. Chem. Pharm.* cxlvi. 140.

making use of a boiling potassium amalgam containing 2 per cent. of this metal.

524 Oxalic acid is not only an oxidation-product of glycollic acid, but also of most of the members of the group of fatty bodies, as also of the allied group of bodies containing less hydrogen. These bodies all yield oxalic acid as a final product when treated with nitric acid. Next to carbon dioxide, oxalic acid is the carbon compound which contains most oxygen. Many organic bodies also yield oxalic acid when they are fused with caustic potash. Acetic acid is only difficultly oxidized by nitric acid, but in alkaline solution it yields large quantities of oxalic acid when treated with potassium permanganate.

*Manufacture.* Scheele first obtained oxalic acid by precipitating salt of sorrel with acetate of lead, and decomposing the product with sulphuric acid. In place of this method, the oxidation of cane-sugar was afterwards employed for the preparation of oxalic acid on a large scale. For this purpose 8 parts of nitric acid of specific gravity 1·38 are gradually added to 1 part of sugar, the mixture heated to the boiling point, and the liquid then evaporated to one-sixth of its bulk, and allowed to cool. The acid, which crystallizes out, is purified by re-crystallization. Instead of refined sugar, a cheaper material, such as brown sugar, molasses, starch-sugar, or starch, may be employed, and the fumes of the oxides of nitrogen evolved may be utilized either by passing them into a sulphuric acid chamber, or they may be again converted into nitric acid by contact with air and water.

This mode of making oxalic acid is, however, no longer in use. In the year 1829, Gay-Lussac found that when cotton-wool, sawdust, sugar, starch, gum, tartaric acid, and other bodies are fused with caustic potash, oxalic acid is formed.[1] The first experiments for utilizing this reaction on the large scale were made by Mr. John Dale of Manchester, by whose skill and perseverance the practical difficulties inherent in the working of the process were successfully removed, leading, in 1856, to the patenting by his firm of a process for the manufacture of oxalic acid from sawdust. Gay-Lussac suggested that cream of tartar should be employed for the preparation of oxalic acid, and at the time this suggestion was a practical one, as this substance was much cheaper than oxalic acid. Mr. Dale found that sawdust was the best material, and that the caustic potash cannot be replaced in the reaction by its cheaper substitute, caustic

[1] *Ann. Chim. Phys.* xli. 398.

soda, as this latter alkali gives but a very small yield. Caustic potash was, however, then too dear to permit its employment on the large scale. If, however, one molecule of potash and two molecules of soda be used, one part of the crystallized acid can be prepared from two parts of sawdust. For this purpose a solution of the alkalis, having a specific gravity of 1·35, is used, and to this sufficient sawdust is added to produce a thick paste, which is then spread on to iron plates and gradually heated. At first, water is given off, the mass then swells up and disengages a quantity of inflammable gas, consisting of hydrogen and hydrocarbons, a peculiar aromatic smell being at the same time noticed. After the temperature has been maintained at 200° for from one to two hours, this part of the process may be considered to be complete. The whole of the woody fibre is decomposed, and the mass, which has a dark-brown colour, is entirely soluble in water, but it contains only from 1 to 4 per cent. of oxalic acid, 0·5 per cent. of formic acid, and no acetic acid. The mass is now exposed still longer to the same temperature, great care being taken to avoid any charring, which would cause a loss of oxalic acid, and as soon as the mass has become dry the operation is complete. The product, which contains about 20 per cent. of anhydrous oxalic acid, combined of course with alkali, is then treated with warm water, when the excess of alkali and the salts of potash and soda are dissolved with the exception of the difficultly-soluble oxalate of soda, which falls to the bottom. The purpose served by the soda is here apparent. The supernatant liquor is drawn off and evaporated to dryness, and the residual mass heated in a furnace in order to drive off the organic matter and recover the alkalis which it contains, and which are again employed, after having been causticized, for acting on fresh sawdust.[1] The oxalate of soda is decomposed

[1] The proportion between the two alkalis in this material is of course different from that contained in the original mixture. In order to bring them quickly into work again, it is necessary to have a rapid method by which their relative amounts can be determined. A series of experiments led Dale to the following simple method of analysis. A given volume of the solution is neutralized with tartaric acid of known strength, and then an equal volume of the acid afterwards added, when acid potassium tartrate is thrown down, its precipitation being aided by stirring. In order to obtain exact results, the solution thus obtained of the acid sodium tartrate must be nearly saturated, or its specific gravity must be 1·09. According to Dale, cream of tartar does not dissolve appreciably in a solution of acid sodium tartrate if the specific gravity does not fall below 1·03. If perfectly accurate results are required, the precipitate must be washed with dilute alcohol. When the acid potassium salt (cream of tartar) is separated out, it is filtered off and washed with a small quantity of water. The filtrate is treated with standard soda, the amount of this alkali used being equal to that contained in the original

by boiling with milk of lime, when caustic soda and insoluble calcium oxalate are formed. The calcium salt is then decomposed by sulphuric acid, the liquid separated from the gypsum and evaporated to crystallization.[1]

Other manufacturers use a mixture of equal molecules of the two alkalis, or, as is now common, only caustic potash, as potash salts are now so much cheaper than formerly. A complete series of experiments made by William Thorn[2] have shown that when spread in thicker layers, the yield is larger the greater the proportion of potash to soda. When thinner layers are employed the yield is still better, but this remains constant whether Dale's proportions are employed or caustic potash alone is used. This observation was, however, made long ago by Mr. Dale. The kind of sawdust employed is of importance. Hard woods yield less acid than soft woods, such as poplar and the coniferas, and as pine sawdust is common, this is almost universally employed.

525 *Properties.* Oxalic acid, $C_2H_2O_4 + 2H_2O$, crystallizes readily in monoclinic prisms. It is easily soluble in water and alcohol, and its acid taste is more powerful than that of any of the other organic acids. It decomposes calcium fluoride, many chromates, and the phosphates and arsenates of several of the heavy metals (Berthollet). When heated with common salt, hydrochloric acid is given off; sodium nitrate is likewise attacked by oxalic acid, acid sodium oxalate being formed in both cases.

Like all strong acids, oxalic acid acts in large doses as a poison. Accidental poisoning with oxalic acid usually results from its being mistaken for Epsom salts. In small doses, however, it is quite harmless, as is seen from the fact that it is contained in garden rhubarb, and many other plants frequently used as articles of food. Doses up to one gram given to a dog did not produce any visible evil effects,[3] nor was any effect noticed in a dog to which twelve grams of normal potassium oxalate were administered for several days (Dale).

liquid. The acid tartrate of potash is next thrown into water, together with the filter paper, and the whole titrated with caustic potash, and the amount of caustic potash contained in the mixture thus directly obtained. Comparative experiments with mixtures containing known quantities of the two alkalis showed that this process, which is a very quick one, yields accurate results. (We are indebted to Mr. Dale for these particulars, which are now published for the first time.)

[1] Schunck, Smith, and Roscoe, *Report Brit. Assoc.* 1861, 120.

[2] *Ber. Entw. Chem. Ind.* ii. 410.

[3] Pfeiffer, *Arch. Pharm.* [3], xiii. 544.

The crystallized acid gradually loses its water of crystallization when placed over sulphuric acid; and when heated to 100° it falls to a white powder which sublimes in white needles at 165°, a portion, however, undergoing decomposition into carbon dioxide and formic acid, or into carbon monoxide and water, the products of decomposition of the latter acid. At higher temperatures this decomposition is complete. If the crystallized acid be allowed to remain in contact with sulphuric acid, glistening, strongly-refracting rhombic pyramids of the anhydrous acid separate out, and these must be quickly dried with filter paper, and washed with ether, as they quickly take up water and fall to powder.[1]

The commercial acid always contains alkalis. In order to purify it, the solution is warmed for some time to 40°, allowed to stand for six hours in a cool place, filtered, the filtrate evaporated to two-thirds, and well stirred during the cooling. The acid which separates out is then washed with cold water and crystallized a second time from boiling water.[2] An acid perfectly free from alkali is best obtained by sublimation, or by the decomposition of the pure methyl or ethyl ether with water.

526 The anhydrous acid is not attacked by chlorine,[3] but it decomposes if water be present, hydrochloric acid and carbon dioxide being formed (Döbereiner). It may be crystallized from hot nitric acid, but when heated with nitric acid of specific gravity 1·4 for some hours to 160°—180°, oxalic acid is completely converted into water and carbon dioxide.[4] It also suffers a similar oxidation at ordinary temperatures. It is only slowly oxidized in aqueous solution in presence of the peroxides of lead and of manganese (Manganese Evaluation, see Vol. II. Part II. p. 26). If the anhydrous acid be rubbed up with five times its weight of lead dioxide the whole mass becomes incandescent. Oxalic acid precipitates finely divided gold from solution of the chloride quickly, especially when heated (Pelletier), and it also decomposes platinic chloride, but only in the sunlight (Döbereiner).

An acidified solution of potassium permanganate decomposes oxalic acid according to the following equation:[5]

$$2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

[1] Reichardt, *Jenaer Zeitsch.* i. 244.
[2] Siebold, *Pharm. Journ. Trans.* [3], vi. 441.
[3] Wöhler and Hallwachs, *Ann. Chem. Pharm.* xcv. 120.
[4] Erlenmeyer, Ligel, and Belli, *ib.* clxxx. 220.
[5] Vernon Harcourt, *Journ. Chem. Soc.* [2], v. 460.

This reaction is employed in order to determine the strength of potassium permanganate solution, which is frequently used in volumetric analysis.

When a dilute solution of oxalic acid is added to uranium nitrate and exposed to the air, a mixture of carbon monoxide and carbon dioxide is evolved.[1]

Oxalic acid, when heated with sulphuric acid, decomposes into carbon monoxide and carbon dioxide (Döbereiner). Phosphorus pentachloride acts upon it as follows:

$$C_2H_2O_4 + PCl_5 = CO + CO_2 + 2HCl + POCl_3.$$

Phosphorus trichloride decomposes the crystallized acid as follows:[2]

$$C_2H_2O_4 + 2H_2O + PCl_3 = CO + CO_2 + 3HCl + P(OH)_3.$$

From these decompositions it is clear that neither the anhydride nor the chloride of oxalyl can be prepared by the reactions by which these compounds are in the case of the other series, usually obtained.

Oxalic acid is reduced to glyoxylic[3] or glycollic acid[4] by the action of zinc and dilute sulphuric acid.

Oxalic acid is used largely in calico-printing, dyeing, the bleaching of flax and straw, and in the preparation of formic acid and of the ethyl ethers, but since the introduction of so many artificial colouring-matters, its use for the two first of these purposes is not now so large as it was formerly.

## OXALATES.

527 The oxalates have been carefully examined by Berzelius,[5] Rammelsberg,[6] and Souchay and Lenssen.[7]

They are very numerous, not only the normal and acid salts of this dibasic acid being known, but the so-called super-acid and double salts also existing.

All the oxalates are decomposed on heating. The products which are thus formed varying according to the chemical nature

[1] See Kamp, *Ann. Chem. Pharm.* cxxii. 113.
[2] Hurtzig and Geuther, *ib.* cxi. 159.
[3] Church, *Journ. Chem. Soc.* [2], i. 301.
[4] Schulze, *Chem. Centralb.* 1862, 609 and 753
[5] Lehrbuch. [6] *Pogg. Ann.* xciii. 24.
[7] *Ann. Chem. Pharm.* xcix. 31 ; c. 308 ; cii. 35 ; ciii. 308 ; cv. 245.

of the metal, or according to the presence or absence of air during the decomposition. The oxalates of the alkali-metals leave a residue of a carbonate, as also do those of the alkaline-earth-metals when they are not too strongly heated. The oxalates of the metals whose carbonates decompose at a high temperature yield, on heating in presence of air, a mixture of the monoxide and dioxide of carbon, together with the oxide of the metal. When air is excluded, the carbon monoxide present may cause a partial reduction of the metallic oxides. Oxalates of metals whose oxides decompose on heating, yield carbon dioxide and the metal. On heating with concentrated sulphuric acid the oxalates decompose in a similar way to the acid itself, no blackening in this case taking place. This serves as an important distinction between oxalic and the other solid vegetable acids.

*Normal Potassium Oxalate*, $C_2O_4K_2 + H_2O$, crystallizes in monoclinic transparent pyramids or prisms, the surfaces of which are usually curved. It is easily soluble in water, and is used in the analysis of pyrolusite, and for other similar purposes.

*Acid Potassium Oxalate*, $C_2O_4KH$, is well-known under the name of salt of sorrel, and occurs in various species of *oxalis* and of *rumex*, in garden rhubarb and various other plants. It forms either anhydrous monoclinic prisms, or crystals belonging to the triclinic system, containing one molecule of water. It is only slightly soluble in cold water, and combines with oxalic acid to form *potassium quadroxalate*, $C_2O_4KH + C_2O_4H_2 + 2H_2O$, the salt crystallizing in large triclinic crystals. Commercial salt of sorrel, used for the removal of inkstains from linen, consists generally of this compound.

The oxalates of potassium were first analysed by Wollaston,[1] and these researches, as well as the analyses of the strontium oxalates by Thomas Thomson, served as an important confirmation of the truth of the law of combination in multiple proportion.

*Normal Sodium Oxalate*, $C_2O_4Na_2$, requires thirty-six parts of water for solution at the ordinary temperature, but is much more easily soluble in hot water, and on cooling separates as a sandy powder or in fine glistening needles. It also occurs in various plants growing in salt marshes, as *salicornia*, *salsola*, &c.

*Acid Sodium Oxalate*, $2C_2O_4HNa + H_2O$, is still less soluble,

[1] *Phil. Trans.* 1808, 99.

and forms hard crystals which are unalterable in the air, and does not form any compound with oxalic acid.

*Normal Ammonium Oxalate*, $C_2O_4(NH_4)_2 + H_2O$, is easily soluble in water, and crystallizes in rhombic prisms. This salt, which is used in chemical analysis, is found in Peruvian guano.

*Acid Ammonium Oxalate*, $2C_2O_4H(NH_4) + H_2O$, is less soluble in water, and crystallizes in rhombic prisms. It forms with oxalic acid the compound, $C_2O_4H(NH_4) + C_2O_4H_2 + 2H_2O$, isomorphous with the corresponding potassium salt.

528 *Calcium Oxalate*, $C_2O_4Ca$, is a compound occurring largely distributed in the vegetable kingdom. It was first discovered by Scheele in the roots of the garden rhubarb, and then in many other plants, and termed by him *calx saccharata*. It is also found in the cells of plants in crystals, and then termed *raphides*. The formation of these will be remarked upon hereafter. Many lichens growing on limestone frequently consist of nearly half their weight of this salt,[1] which is also found on the marble of the Parthenon, and was described by Liebig as a new mineral under the name of Thierschite, this being probably formed by the action of a lichen. Calcium oxalate is also found in various animal liquids, as in urine. It also occurs in urinary deposits, being known as the mulberry calculus, from its peculiar appearance.

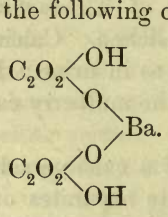
If a neutral solution of a calcium salt be mixed with one of an oxalate, calcium oxalate separates out, even in very dilute solution, as a crystalline precipitate which is insoluble in water and acetic acid, though dissolving in nitric and hydrochloric acid, &c. This reaction, which is much used to distinguish oxalic from phosphoric acid, and also for the detection and quantitative determination of calcium, was noticed soon after the discovery of oxalic acid by various chemists, and recommended by them as the best means of detecting lime, but others believed that oxalic acid was an unreliable reagent, as in presence of mineral acids no precipitate made its appearance. Darracq then showed that, on neutralization with ammonia, lime could always be detected by means of oxalic acid.

Precipitated calcium oxalate contains water, and after drying at 100° has the composition $C_2O_4Ca + H_2O$, the precipitate obtained from boiling solution having also the same composition. The same hydrate is obtained in monoclinic laminæ when

[1] Braconnot, *Ann. Chim. Phys.* xxviii. 318.

the salt is dissolved in boiling hydrochloric acid or nitric acid and allowed to cool. It becomes anhydrous at 180°, but on exposure to air again absorbs water. A solution in an excess of cold hydrochloric acid deposits on standing tetragonal tables, having the composition $C_2O_4Ca + 3H_2O$, and this compound is also found in the cells of plants, being probably deposited from a saccharine solution,[1] as Scheibler has proved that it easily dissolves in the juice of mangel-wurzel. Vesque[2] has also shown that it readily dissolves in glucose and dextrine, and Monier[3] obtained it crystalline by allowing a solution of oxalic acid to stand in contact with one of lime dissolved in sugar, and these crystals exactly resembled the raphides.

An acid calcium oxalate is not known, although barium and strontium yield, in addition to the very insoluble normal salts, acid oxalates, $C_2O_4Ba + C_2O_4H_2 + 2H_2O$, and $C_2O_4Sr + C_2O_4H_2 + 2H_2O$. The acid oxalates are easily soluble in water, but the solutions decompose, especially on warming, with separation of the normal salt. They are probably molecular compounds, analogous to potassium quadroxalate. They may, however, be really acid salts having the following constitution:




529 *Lead Oxalate*, $C_2O_4Pb$, is a heavy precipitate, insoluble in water, which is, however, soluble in nitric acid, and also in a solution of sal-ammoniac and other ammoniacal salts. When heated in absence of air to 300° it decomposes according to the following equation:[4]

$$2C_2O_4Pb = 3CO_2 + CO + Pb_2O.$$

*Silver Oxalate*, $C_2O_4Ag_2$, is a white precipitate which decomposes at 110°, and detonates when quickly heated.

*Mercuric Oxalate*, $C_2O_4Hg$, can only be obtained in the pure state by adding mercuric nitrate to a very large excess of a

[1] Scheibler, *Zeitsch. Chem.* [2], i. 62.
[2] Vesque, *Compt. Rend.* lxxviii. 149.
[3] Monier, *ib.* lxiii. 1013; lxxviii. 300.
[4] Pelouze, *Ann. Chim. Phys.* [3], iv. 104; see also Maumené, *Compt. Rend.* lxxi. 797 and 837.

solution of oxalic acid. The dry salt explodes with great violence on percussion.

*Ferrous Oxalate*, $C_2O_4Fe$, occurs in the brown-coal formation and is termed by the mineralogists *humboldtine*, or *oxalite*. It contains $1\frac{1}{2}$ molecules of water, and often occurs in capillary forms, but also in botryoidal masses, and in plates, with a fibrous or compact structure. If a solution of green vitriol be mixed with oxalic acid or an oxalate, ferrous oxalate is thrown down as a heavy bright yellow powder, insoluble in water, and only slightly soluble by dilute acids. When a solution of ferric hydroxide in aqueous oxalic acid is exposed to the action of sunlight, carbon dioxide is evolved, and the ferrous salt is precipitated in fine lemon-coloured glistening crystals. This substance has, like the precipitated salt, the composition $C_2O_4Fe + 2H_2O$. On heating it leaves a very finely divided oxide of iron, which serves as a useful polishing powder for optical purposes. It has been proposed by Draper [1] to employ the above reaction as a means of measuring the chemical action effected by sunlight. It has also been used as a sensitive photographic agent in the production of Herschel's cyanotype.

If a solution of a normal oxalate be added to one of ferric chloride, a yellow precipitate is slowly formed, which is probably normal ferric oxalate. This compound is also formed when ferric hydroxide is treated with a solution of oxalic acid. An excess of the latter must be avoided, as the salt dissolves readily in this acid.

530 *Oxalates of Antimony.* This metal only forms insoluble basic oxalates; but, on the other hand, the double salts of antimony and the alkali metals dissolve in water, and are of interest, as, unlike most antimony salts, they are not decomposed by water, for which reason probably they might be employed as a substitute for tartar emetic in dyeing and calico-printing.

*Antimony Potassium Oxalate*, $(C_2O_4)_3SbK_3 + 6H_2O$, is obtained by dissolving antimonic acid in a hot solution of acid potassium oxalate, when it deposits in monoclinic crystals.

*Antimony Sodium Oxalate*, $(C_2O_4)_3SbNa_3 + C_2O_4Na_2 + 10H_2O$, is prepared in a similar way to the potassium compound, and is deposited in the form of glistening crystals.[2] Other double salts have also been described.

Arsenic trioxide seems to form similar double salts.

[1] *Phil. Mag.* [4], xviii. 91.
[2] Svenssen, *Ber. Deutsch. Chem. Ges.* iii. 314.

## ETHEREAL SALTS OF OXALIC ACID.

531 *Methyl Oxalate*, $C_2O_4(CH_3)_2$, is a solid body, first prepared by Dumas and Péligot[1] by distilling methyl alcohol with sulphuric and oxalic acids. According to Weidmann and Schweizer,[2] salts of sorrel may be advantageously employed in place of the acid. The same chemists found that the ether is formed by heating wood-spirit with oxalic acid. According to Erlenmeyer,[3] it is best obtained by dissolving anhydrous oxalic acid in boiling methyl alcohol, and bringing the crystals which are deposited, on to a vacuum filter, and washing with cold water until the liquid which runs off no longer gives the iodoform reaction.

Methyl oxalate crystallizes in rhombic tables; it melts at 51°, and boils at 162°. When brought in contact with water it decomposes, slowly in the cold and more quickly on warming, into oxalic acid and methyl alcohol.

*Ethyl Oxalate*, $C_2O_4(C_2H_5)_2$. This ether is a liquid, and was first obtained by Bergmann by distilling together oxalic acid and spirit of wine. It was soon afterwards investigated by other chemists, who gave a variety of methods for its preparation.[4] It is best obtained according to the method given by Frankland and Duppa.[5] A mixture of three parts of anhydrous oxalic acid and two parts of absolute alcohol is slowly heated for some time in a tubulated retort to 100°, and afterwards the temperature raised to 125°—130°, when the vapour of two parts of absolute alcohol is passed in. The product is then purified by fractional distillation.

Ethyl oxalate is a liquid possessing a slightly aromatic smell, boiling at 186°, and having at 15° a specific gravity of 1·0824. It behaves in a similar way with water to methyl oxalate. This substance is used for the separation and purification of the amines (Vol. III. Part I. p. 221), and for the synthetical preparation of various acids of the lactic acid group. Ethyl oxalate, when exposed

[1] *Ann. Chim. Phys.* lviii. 44; *Ann. Chem. Pharm.* xv. 32.

[2] *Pogg. Ann.* xliii. 602; see also Wöhler, *Ann. Chem. Pharm.* lxxxi. 376.

[3] *Rep. Pharm.* [2], xxiii. 432; see also Cahours and Demarçay, *Bull. Soc. Chim.* [2], xxix. 468.

[4] Thénard, *Mém. Soc. d'Acueil.* ii. 11; Bauhof, *Schweig. Journ.* xix. 308; Dumas and Boullay, *Journ. Pharm.* xiv. 113; Mitscherlich, *Lehrb;* Löwig, *Journ. Prakt. Chem.* lxxxiii. 129; lxxxiv. 1; Kolbe and Kalle, *Ann. Chem. Pharm.* cxix. 173.

[5] *Ib.* 1.

to the action of chlorine in sunlight, yields, as the last product, perchlorethyl oxalate, $C_2O_4(C_2Cl_5)_2$, an odourless body, crystallizing in rectangular prisms, which melt at 144°.[1] Ethyl oxalate decomposes on repeated distillation into carbonyl chloride, carbonic oxide, and triacetyl chloride. When it is heated with sodium, carbon monoxide is formed and ethyl carbonate produced.[2] The same decomposition takes place when sodium ethylate is employed, other products being also produced.[3]

*Acid Ethyl Oxalate*, or *Ethyl Oxalic Acid*, $C_2O_4(C_2H_5)H$. The potassium salt of this acid is obtained by the action of a solution of caustic potash in absolute alcohol on ethyl oxalate, when this compound separates out in laminæ. If these be dissolved in aqueous alcohol, some potassium oxalate remains behind, and, on addition of the requisite quantity of sulphuric acid to the filtrate, potassium sulphate is thrown down, whilst ethyl oxalic acid remains in solution. If this be diluted with water, saturated with barium carbonate, and the filtrate evaporated on the water-bath to a small bulk, crystals of barium ethyl oxalate are obtained. By decomposing the aqueous solution of this salt with dilute sulphuric acid, free ethyl oxalic acid is obtained. It is very unstable, decomposing readily into alcohol and oxalic acid, even when the solution is evaporated in a vacuum.[4]

*Ethyl Oxalyl Chloride*, $C_2O_2(OC_2H_5)Cl$, is formed by the action of phosphorus oxychloride on potassium ethyl oxalate. It is a fuming mobile liquid, possessing a suffocating odour, boiling at 140°, and exhibiting the usual properties of the acid chlorides.[5]

Amongst other ethereal salts of oxalic acid the following may be mentioned:

| | | B. P. |
|---|---|---|
| [6] Methyl-ethyl-oxalate, | $C_2O_4(CH_3)(C_2H_5)$ . | 160—170° |
| [7] Propyl oxalate, | $C_2O_4(C_3H_7)_2$ . . . | 209—211° |
| [7] Isobutyl oxalate, | $C_2O_4(C_4H_9)_2$ . . . | 244—246° |
| [8] Amyl oxalate, | $C_2O_4(C_5H_{11})_2$ . . | 265° |

[1] Malaguti, *Ann. Chim. Phys.* [2], lxxiv. 299.
[2] Ettling, *Ann. Chem Pharm.* xix. 17.
[3] Geuther, *Zeitsch. Chem.* [2], iv. 656; Cranston and Dittmar, *Journ. Chem. Soc.* [2], vii. 441.
[4] Mitscherlich, *Pogg. Ann.* xxxiii. 332.
[5] Henry, *Ber. Deutsch. Chem. Ges.* iv. 598.
[6] Chancel, *Jahresb.* 1850, 469.
[7] Cahours, *Compt. Rend.* lxxvii. 749 and 1408.
[8] Balard, *Ann. Chim. Phys.* [3], xii. 309; Delffs, *Jahresb.* 1854, 26.

## AMIDO-COMPOUNDS OF OXALYL.

532 *Oxamide*, $C_2O_4(NH_2)_2$. This body was obtained by Bauhof in 1817, by acting upon ethyl oxalate with aqueous ammonia.[1] He, however, considered it to be "an intimate triple compound, consisting of oxalic acid, alcohol, and ammonia." Liebig,[2] in 1834, showed that the body thus prepared is identical with the oxamide obtained by Dumas in 1830 by distillation of ammonium oxalate.[3]

In order to prepare it, ethyl oxalate, which need not necessarily be perfectly pure, is shaken up with aqueous ammonia. The liquid becomes warm, and oxamide separates out as a white precipitate. Oxamide is also formed, together with other products, by the action of nitric acid on potassium ferrocyanide,[4] as well as when potassium cyanide is warmed with manganese dioxide and a small quantity of sulphuric acid, or when aqueous solutions of hydrocyanic acid and hydrogen dioxide are allowed to stand for some days.[5]

Oxamide is a light crystalline powder, almost insoluble in water, alcohol, and ether. When heated with alcohol for a few days to 210°—220°, it is converted into small rectangular prisms with pyramidal terminations.[6] It is perfectly neutral. When boiled with water and mercuric oxide, the compound $2C_2O_2(NH_2)_2 + HgO$ is formed as a white insoluble powder.[7] When oxamide is heated with water and strong acids or alkalis, it forms oxalic acid and ammonia.

*Ethyl Oxamide*, $CO.NH(C_2H_5).CO(NH_2)$, is easily formed by the action of aqueous ammonia on ethyl oxamethane (p. 121). It is easily soluble in water, alcohol, and ether, melts at 202°—203°, but sublimes at a lower temperature in fine woolly crystalline masses (Wallach and West).

533 *Diethyl Oxamide*, $C_2O_2(NH.C_2H_5)_2$, was first prepared by Wurtz by acting with ethylamine on ethyl oxalate.[8] It is best prepared by mixing a well-cooled, concentrated aqueous

[1] *Schweig. Journ.* xix. 313.
[2] *Ann. Chem. Pharm.* ix. 11 and 129.
[3] *Ann. Chim. Phys.* xliv. 129; liv. 240.
[4] Playfair, *Phil. Trans.* 1849, ii. 477; see also Vol. II. Part II., p. 115.
[5] Attfield, *Journ. Chem. Soc.* [2], i. 94.
[6] Geuther, *Ann. Chem. Pharm.* cix. 72.
[7] Dessaignes, *Ann. Chim. Phys.* [3], xxxiv. 143.
[8] *Ib.* xxx. 490.

solution of ethylamine with ethyl oxalate.[1] This compound crystallizes in needles which are difficultly soluble in water but dissolve more easily in alcohol, and it volatilizes without decomposition. By acting upon it with phosphorus pentachloride the following compounds are obtained:

$$\begin{array}{l} CCl_2.N(C_2H_5)H \\ | \\ CCl_2.N(C_2H_5)H \end{array} \qquad \text{and} \qquad \begin{array}{l} CCl.N(C_2H_5)H \\ \| \\ CCl.N(C_2H_5)H. \end{array}$$

These have not yet been prepared in the pure state. Their probable constitution is, however, indicated by the fact that they may be again converted into diethyl oxamide by means of water. If, however, the product be allowed to stand for some days with the phosphorus oxychloride which has been formed, decomposition occurs, and the tertiary amine, *chloroxalethyline*, $C_6H_9ClN_2$, is formed, the hydrochloride of which remains behind if the phosphorus oxychloride be distilled off under diminished pressure. This substance crystallizes in prisms, and yields a crystalline platinichloride. By distillation with caustic potash the free base is obtained as an oily narcotic-smelling liquid, boiling at 217°—218°, and having an alkaline reaction and crystallizing when strongly cooled. It combines with various metallic salts, forming crystalline compounds, and with the iodides of the alcohol radicals to form compound ammonium iodides, such as $C_6H_9ClN_2.CH_3I$, crystallizing in prisms, and yielding a strongly alkaline hydroxide on treatment with silver oxide.

By the action of sodium on a solution of chloroxalethyline in petroleum oil, *dioxalethyline*, $C_{12}H_{18}N_4$, is formed, a thick liquid, having an alkaline reaction, and boiling above 300°.[2]

*Oxalethyline*, $C_6H_{10}N_2$, is formed when the chlorine-compound is heated with hydriodic acid and amorphous phosphorus, and the product decomposed by caustic soda. It is a thick, transparent, oily liquid, boiling at 212°—213°, and having a strongly narcotic smell.[3] Most of its salts crystallize well, and like chloroxalethyline it is a tertiary base.[4]

Oxalethyline is poisonous, producing the same symptoms as atropine, the poisonous principle of the deadly nightshade, especially the dilatation of the pupil, though it does not act so powerfully as this alkaloid. Chloroxalethyline, on the other

[1] Wallach, *Ann. Chem. Pharm.* clxxxiv. 33.
[2] Wallach and Oppenheim, *Ber. Deutsch. Chem. Ges.* x. 1193.
[3] Wallach and Stricker, *ib.* xiii. 511.
[4] Wallach and E. Schultze, *ib.* 514.

hand, does not produce these symptoms, and acts upon the brain in a similar way to chloral hydrate.[1]

The oxamides of the other alcohol radicals give compounds similar to those which have been now described.[2]

534 *Oxamic Acid*, $CO(NH_2)CO_2H$, was discovered in 1842 by Balard,[3] who obtained it by heating acid ammonium oxalate. Its ammonium salt is formed when oxamide is boiled for some time with aqueous ammonia :[4]

$$\begin{matrix} CO.NH_2 \\ | \\ CO.NH_2 \end{matrix} + H_2O = \begin{matrix} CO.NH_2 \\ | \\ CO.ONH_4. \end{matrix}$$

Free oxamic acid is obtained from this salt by decomposition with hydrochloric acid. It is deposited as a fine crystalline powder, which dissolves at 14° in seventy-one parts of water, and melts at 173°, yielding oxamide and the products of decomposition of oxalic acid. If the acid be boiled with water it combines with it to form acid ammonium oxalate. It is monobasic, and forms crystalline salts.[5]

*Ethyl Oxamate*, or *Oxamethane*, $CO(NH_2)CO_2(C_2H_5)$, was discovered in 1828 by Boullay and Dumas,[6] and then examined by the latter chemist, who termed it oxamethane,[7] as well as by Liebig,[8] who considered it to be "an oxamate of ammonia." It is best prepared by dissolving ethyl oxalate in two to three volumes of alcohol, and gradually adding to this liquid, well cooled with ice, the requisite quantity of ammonia in alcoholic solution.[9]

It is easily soluble in water and alcohol, and crystallizes in flat, long, rhombic needles, which melt at 114°—115°.[10] It can be distilled without decomposition, and is quickly converted by ammonia into oxamide.

535 *Ethyl Oxamic Acid*, $CO.NH(C_2H_5)CO_2H$, was obtained by Wurtz[11] by heating acid ethylamine oxalate to 180°. Heintz[12] discovered it amongst the products of the action of ethylamine

[1] H. Schultz, *Ber. Deutsch. Chem. Ges.* xiii. 2353.
[2] Wallach and E. Schultze, *ib.* xiv. 420.
[3] *Ann. Chim. Phys.* [3], iv. 93.
[4] Toussaint, *Ann. Chem. Pharm.* cxx. 237.
[5] Engström, *Journ. Prakt. Chem.* lxviii. 433 ; Bacaloglo, *ib.* lxxxi. 379.
[6] *Ann. Chim. Phys.* xxxvii. 37.
[7] *Ib.* liv. 241.
[8] *Ann. Chem. Pharm.* ix. 129.
[9] *Journ. Prakt. Chem.* [2], x. 193.
[10] Wallach, *Ann. Chem. Pharm.* clxxxiv. 8.
[11] *Ann. Chim. Phys.* [3], xxx. 490.
[12] *Ann. Chem. Pharm.* cxxvii. 43.

on ethyl oxalate. Wallach and West[1] have shown that the ethyl ether is formed in this reaction, and is best obtained by mixing a solution of the amine in absolute alcohol with ethyl oxalate, allowing the mixture to stand for some time, and then distilling the alcohol off and fractionating the residue in order to separate the excess of ethyl oxalate. Diethyl oxamide crystallizes out from the higher boiling portions on cooling, and its separation may be aided by placing it in a freezing mixture. It is then brought on to a vacuum filter and freed from the liquid. This latter, which is *ethyl oxamethane*, $CO.NH(C_2H_5)CO_2.C_2H_5$, boils at 244°—246°. When pure it has a faint smell, but usually smells of the carbamines. It is decomposed by water, and more readily by bases with formation of ethyl oxamic acid. This latter substance is easily soluble in water, crystallizes in six-sided laminæ, melts at 120°, and sublimes, when strongly heated, in thin, elastic needles.

*Diethyl Oxamic Acid*, $CO.N(C_2H_5)_2CO_2H$. The ethyl ether of this acid is formed by acting with diethylamine on ethyl oxalate. It is a liquid boiling at 160°.[2] When heated with milk of lime this ether yields the calcium salt of the acid. From this the free acid can be obtained by the addition of oxalic acid. It is easily soluble, and crystallizes in monoclinic prisms, which, on heating, fuse and easily sublime in thin needles.[3]

Besides the ethylated oxamides and oxamic acids above described, a large number containing other or two different alcohol radicals have been prepared. Their mode of preparation, reactions, &c., correspond to those of the ethyl compounds.

*Isodiethyloxamide*, $CO(NH_2)CON(C_2H_5)_2$, is obtained when the ethyl ether of the foregoing compound is treated with concentrated aqueous ammonia. It crystallizes in large, thick prisms, fuses at 126°—127°, and boils at 266°—268°; it begins, however to sublime at 100°. When heated with phosphorus pentoxide the nitril of diethyl oxamic acid, $CN.CO(N.C_2H_5)_2$, is formed. It is a faintly smelling liquid, boiling at 219°—220°.

*Triethyl Oxamide*, $CO(NH.C_2H_5)CON(C_2H_5)_2$, is formed when the ethyl ether of diethyl oxamic acid is treated with ethylamine. It is a liquid soluble in water, boiling at 257°—259°.[4]

*Dihydroxyl Oxamide*, $C_2O_2(NH.OH)_2$, is obtained by the addition of ethyl oxalate to a boiling alcoholic solution of hydroxyl-

[1] *Ann. Chem. Pharm.* clxxxiv. 57.
[2] Hofmann, *Compt. Rend.* lii. 902.
[3] Heintz, *Ann. Chem. Pharm.* cxxvii. 43.
[4] Wallach, *Ber. Deutsch. Chem. Ges.* xiv. 735.

amine. On cooling, the compound $C_2O_2(NH.OH)_2.NH_2OH$ separates out in thin laminæ, which decompose on addition of hydrochloric acid, and on evaporation yield a crystalline mass which is purified by recrystallization. It is difficultly soluble in water, crystallizes in small prisms, and acts as a weak dibasic acid. Both it and its salts deflagrate on heating.[1]

The *carbamide compounds of oxalic acid* were first obtained by oxidizing uric acid. They will be described under that acid.

## The Nitrils of Oxalic Acid.

536 Dibasic oxalic acid forms the two following nitrils :

Cyanformic Acid. $\begin{matrix} CN \\ | \\ CO.OH. \end{matrix}$ Oxalonitril, or Cyanogen. $\begin{matrix} CN \\ | \\ CN. \end{matrix}$

*Cyanformic Acid,* $CN.CO_2H$. This compound, commonly called *cyancarbonic acid,* is not known in the free state, but Weddige has prepared several of its ethers by heating oxamic ethers with phosphorus pentoxide to 150°—170° :[2]

$$\begin{matrix} CO.NH_2 \\ | \\ CO.OC_2H_5 \end{matrix} = \begin{matrix} CN \\ | \\ CO.OC_2H_5 \end{matrix} + H_2O.$$

*Ethyl Cyanformate,* $CN.CO_2C_2H_5$, is also formed by the action of phosphorus pentachloride on ethyl oxamate.[3] It is a mobile, highly refracting, ethereal smelling liquid, boiling at 116°. Nascent hydrogen reduces it to glycocol (Wallach). When heated with water it decomposes with formation of hydrocyanic acid, carbon dioxide, and alcohol. Concentrated hydrochloric acid converts it into oxalic acid, but the gaseous acid transforms it into its polymeride, *ethyl paracyanformate,* the probable formula of which is $C_3N_3(CO.OC_2H_5)_3$. This body is deposited in glistening crystals, scarcely soluble in water, and dissolving only with difficulty in boiling alcohol. The crystals melt at 165°, and decompose when more strongly heated. Cold caustic potash decomposes the ether with formation of *potassium paracyanformate,* $C_3N_3(CO_2K)_3$, crystallizing in long needles. Hydrochloric acid added to this substance liberates the free acid,

[1] Lossen, *Ann. Chem. Pharm.* cl. 314.
[2] *Journ. Prakt. Chem.* [2], x. 193.
[3] Wallach, *Ann. Chem. Pharm.* clxxxiv. 12.

as a white, light, crystalline powder, very difficultly soluble in water, and decomposing when strongly heated. On boiling with water, oxalic acid and ammonia are formed.

*Ethyl Isocyanformate*, $CN.CO_2(C_2H_5)$. This body, a compound belonging to the carbamines (Part I., p. 159), was termed by Salomon isocyancarbonic ether. He obtained it by acting with alcoholic potash on ethyl carbamate and chloroform, but he could not examine it further as, unfortunately, he inhaled some of its vapour, which produced so serious an effect on his lungs that convulsions ensued, and although he recovered, his health was so much shattered that he gave up the further examination of this unpleasant substance. He only further remarks that it possesses the peculiar smell of the carbamines.[1]

537 *Oxalonitril*, or *Cyanogen*, $C_2N_2$. This body, already described in the first volume, must here again be mentioned, on account of its relationship with oxalic acid. It was discovered in 1815 by Gay Lussac, who showed that the cyanides of mercury and silver are decomposed when heated into cyanogen and the metal.[2] It is likewise formed when oxamide is heated with phosphorus pentoxide,[3] and also by passing the induction spark from carbon poles in an atmosphere of nitrogen.[4]

In order to prepare it, well-dried cyanide of mercury is heated in a tube or small retort of hard glass, and the gas collected over mercury. It is colourless, possesses a peculiar smell resembling peach-kernels, and is easily inflammable, burning with a bluish purple-mantled flame. Its specific gravity is 1·8064. By pressure and by cooling it is converted into a liquid which boils at $-20°{\cdot}7$, and at $17°{\cdot}2$ has a specific gravity of 0·866 (Faraday). Hofmann has described a simple apparatus for liquefying cyanogen.[5] On further cooling it solidifies to a radiating crystalline mass, which melts at $-34°{\cdot}4$. Water dissolves about 4·5 times its volume of the gas; the solution, however, soon becomes yellow, and then brown, depositing brown flakes of azulmic acid, $C_4H_5N_5O$, whilst the liquid is found to contain ammonium oxalate, ammonium oxamate, ammonium carbonate, oxamide, and urea.[6] In presence of small traces of aldehyde

[1] *Journ. Prakt. Chem.* [2], ix. 298.
[2] *Ann. Chim.* xcv. 172.
[3] Bertagnini, *Ann. Chem. Pharm.* civ. 176.
[4] Morren, *Compt. Rend.* xlviii. 342.
[5] *Ber. Deutsch. Chem. Ges.* iii. 663.
[6] Vauquelin, *Ann. Chim. Phys.* xxii. 132; Wöhler, *Pogg. Ann.* xv. 627; Pelouze and Richardson, *Ann. Chem. Pharm.* xxvi. 63.

scarcely anything but oxamide is formed.[1] The same compound is obtained when strong hydrochloric acid is saturated with cyanogen.[2]

Dry sulphuretted hydrogen does not act upon cyanogen, but in presence of aqueous vapour the two following products are formed.[3]

538 *Thioxalenide*, or *Hydroflavic Acid*, $CN.CS.NH_2$, crystallizes in yellow needles, soluble in water and alcohol.

*Thio-oxamide*, or *Hydrorubianic Acid*, $(CS)_2(NH_2)_2$, forms yellowish-red crystals, difficultly soluble in water, but dissolving more readily in hot alcohol.

Both these compounds decompose on boiling with dilute alkalis and acids with formation of oxalic acid, ammonia, and sulphuretted hydrogen.

Aqueous ammonia absorbs cyanogen gas rapidly, and the solution soon forms the same products as are found in aqueous solution.[4]

Dry ammonia gas combines with cyanogen to form *hydrazulmin*, $C_4H_6N_6$, a jet black, glistening amorphous mass, which forms with water the above-named azulmic acid or *hydrazulmoxin* and ammonia. This body has a special interest because it stands in close relation to uric acid (Jacobsen and Emmerling).

*Paracyanogen*, (CN)x, is always formed in small quantity when the cyanides of silver and mercury are heated as also when hydrazulmin is heated. It is a brown amorphous powder which, when heated for some time, volatilizes with formation of cyanogen.

## THE PROPYLENE COMPOUNDS.

539 *Propylene*, or *Methyl Ethylene*, $CH_3CH{=}CH_2$. This gas was discovered by J. W. Reynolds, who obtained it together with other products by passing the vapour of amyl alcohol through a tube heated to moderate redness. That it is formed in this

[1] Liebig, *Ann. Chem. Pharm.* cxiii. 246.
[2] Volhard, *ib.* clviii. 118.
[3] Gay Lussac, *Ann. Chim.* xcv. 136; Poret, *Ann. Phil.* xiii. 363; Wöhler, *Pogg. Ann.* iii. 177; Völckel, *Ann. Chem. Pharm.* xxxviii. 314.
[4] Wöhler, *Pogg. Ann.* iii. 177; xii. 253; Jacobsen and Emmerling, *Ber. Deutsch. Chem. Ges.* iv. 947.

process in considerable quantity was shown by Reynolds, by preparing the dichloride and dibromide, which he analysed.[1] About the same time Hofmann found that this gas occurs amongst the products of the action of a red-heat upon valeric acid.[2] Pure propylene was first prepared by Berthelot and de Luca by acting with zinc and dilute sulphuric acid, or with mercury and fuming sulphuric acid on allyl iodide, $C_3H_5I$.[3] In the last case allyl-mercury iodide, $C_3H_5HgI$, is formed, and this is decomposed by strong acid or sulphuretted hydrogen with formation of propylene.[4] Allyl iodide also yields pure propylene when its solution in glacial acetic acid is allowed to run on to granulated zinc.[5] Instead of glacial acetic acid, alcohol may also be employed,[6] and, according to Niederist, this latter method is to be preferred.[7] The following is the reaction which then occurs:

$$C_3H_5I + C_2H_5.OH + Zn = C_3H_6 + C_2H_5OZnI.$$

Propylene is also obtained by heating secondary propyl iodide with alcoholic potash,[8] as well as by allowing a mixture of isopropyl alcohol and 2·6 times its volume of zinc chloride to stand for twenty-four hours and then heating it.[9] Propylene is also obtained in considerable quantities, but mixed with hydrogen, when glycerin, $C_3H_8O_3$, is mixed with zinc dust, to form a thick paste, and the mixture heated.[10]

By the action of zinc ethyl on tetrachlormethane, the following reaction takes place:[11]

$$2CCl_4 + 3Zn(C_2H_5)_2 = 2C_3H_6 + 2C_2H_4 + 2C_2H_5Cl + 3ZnCl_2.$$

Zinc ethyl acts in a similar way on bromoform:[12]

$$CHBr_3 + Zn(C_2H_5)_2 = C_3H_6 + C_2H_5Br + ZnBr_2.$$

Propylene also occurs frequently amongst the products of decomposition of organic bodies by heat, and is, therefore, found in coal gas.

Propylene gas possesses an alliaceous smell, has a specific

[1] *Quart. Journ Chem. Soc.* iii. 111.
[2] *Ib.* 121.
[3] *Ann. Chim. Phys.* [3], xliii. 257; *Ann. Chem. Pharm.* xcii. 306.
[4] Linnemann, *ib.* Suppl. iii. 262.
[5] *Ib.* clxi. 54.
[6] Gladstone and Tribe, *Journ. Chem. Soc.* 1874, 211.
[7] *Ann. Chem. Pharm.* cxcvi. 358.
[8] Erlenmeyer, *ib.* cxxxix. 228.
[9] Friedel and Silva, *Compt. Rend.* lxxvi. 1594.
[10] Claus and Kerstein, *Ber. Deutsch. Chem. Ges.* ix. 695.
[11] Beilstein and Rieth, *Ann Chem. Pharm.* cxxiv. 242.
[12] Beilstein and Alexejew, *Jahresb.* 1864, 470.

gravity of 1·498, and is not liquefied at – 40°, but under increased pressure it can be condensed to a liquid (Berthelot and de Luca). One volume of water absorbs at [1]

$$t^\circ = 0{\cdot}446506 - 0{\cdot}022075\ t + 0{\cdot}0005388\ t^2.$$

Absolute alcohol dissolves about twelve volumes of the gas, and concentrated sulphuric acid 200 volumes, with formation of isopropyl sulphuric acid (Berthelot).

540 *Propylene Alcohol*, or *Propylene Glycol*, $C_3H_6(OH)_2$, was obtained by Wurtz from propylene bromide in the same way as ethylene alcohol from ethylene bromide.[2] It is also formed when propylene bromide, mixed with about thirty-six parts of water, is boiled in connection with a reversed condenser until it is all dissolved. In this way about 43 per cent. of the theoretical yield is obtained, whilst at the same time a considerable quantity of dimethyl ketone is formed. The production of these compounds is explained by the following equations: [3]

$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_2Br \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2OH \end{array} + 2HBr.$$

$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_2Br \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} = 2HBr.$$

Propylene glycol is a thick liquid having a sweetish taste, and boiling at 188°·4 (Linnemann). At 0° it has a specific gravity 1·054.

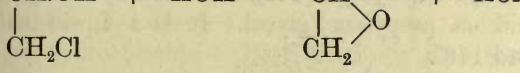
Propylene glycol can also be obtained from glycerin, $CH_2(OH).CH(OH).CH_2(OH)$. If this body be gradually brought in contact with sodium amalgam until one molecule of glycerin has been employed for one atom of sodium, a transparent gum-like mass is formed, and this on heating first gives off water, and then evolves a gas, whilst a liquid passes over from which glycol may be separated by fractional distillation. The quantity obtained amounts to 10 per cent. of the glycerin employed. In

[1] Than, *Ann. Chem. Pharm.* cxxiii. 187.
[2] *Ann. Chim. Phys* [3], lv. 438; lxiii. 124.
[3] Niederist, *Ann. Chem. Pharm.* cxcvi. 357.

place of the amalgam, caustic soda may also be used. The residue contains the sodium salts of several acids, and many other liquids are found in the distillate together with glycol.[1] Amongst these, methyl alcohol, ethyl alcohol, propyl alcohol, and an hexylene have already been detected.[2] When propylene glycol is heated with zinc chloride, propionaldehyde is formed, and this is also produced when the glycol containing a trace of hydrochloric acid is heated to 215°—220°.[3]

Propylene glycol contains an asymmetric carbon atom, and Le Bel has successfully endeavoured to convert it into an optically active substance, making use for this purpose of the action of *bacterium termo* on a three per-cent. solution of the glycol to which the necessary bacterium-food had been added. After the fermentation had proceeded for several months, propionic and lactic acids were found in the liquid, whilst the glycol, which had not been attacked, exhibited levro-rotatory properties.[4]

541 *Propylene Oxide*, $C_3H_6O$. This body, isomeric with propionaldehyde and with acetone, is formed by the action of caustic potash on propylene chlorhydrate :[5]



It is a mobile liquid having an ethereal smell and a pungent taste, and boiling at 35°. Its specific gravity at 0° is 0·859, and that of its vapour 2·054. It is soluble in water, but insoluble in saline solutions. When heated with a solution of magnesium chloride, magnesia separates out, and when sodium amalgam is added to its aqueous solution, it is converted into isopropyl alcohol.[6] The oxide prepared from active propylene glycol is dextro-rotatory, and is the most volatile of all optically-active compounds which have as yet been prepared.

*Propylene Chlorhydrin*, $CH_3.CH(OH)CH_2Cl$, is formed by saturating propylene glycol with hydrochloric acid. The operation must at last be conducted in the water-bath, and the product distilled. The distillate is saturated with sodium carbonate,

[1] Belhoubek, *Ber. Deutsch. Chem. Ges.* xii. 1872.
[2] Jernbach, *Bull. Soc. Chim.* xxxiv. 146.
[3] Linnemann, *Liebig's Ann.* cxcii. 61.
[4] *Compt. Rend.* xcii. 532.
[5] Oser, *Ann. Chem. Pharm.* Suppl. i. 253.
[6] Linnemann, *ib.* cxl. 178.

and the oily layer, which separates out, rectified.[1] The same compound is also formed by the union of propylene and hypochlorous acid.[2] It is an ethereal smelling liquid possessing a sweet though pungent taste, boiling at 127°, and having at 0° a specific gravity of 1·1302. On oxidation it is converted into monochloracetone,[3] and hence it is chlorisopropyl alcohol.

*Propylene Dichloride*, $C_3H_6Cl_2$, is not only formed by the direct union of propylene and chlorine, but is obtained, together with other substitution-products, by the action of chlorine on propane [4] and isopropyl chloride. In the latter case, the isomeric dimethyl methylene dichloride is also formed and in larger quantity, but if a small quantity of iodine be present, more of the former body is produced, and when isopropyl chloride is heated with iodine monochloride to 120°, no dimethyl methylene dichloride is formed, the whole product being propylene dichloride, mixed with small amounts of other bodies.[5]

Propylene dichloride is an oily liquid, smelling like ethylene chloride, boiling at 96°·8, and having a specific gravity at 14° of 1·1656.[6] On heating with alcoholic potash, it yields two isomeric monochlorpropylenes which will be afterwards described.

*Propylene Bromhydrin*, $C_3H_6Br(OH)$, is formed by acting with hydrobromic acid on propylene glycol. It is a liquid boiling between 145° and 148°.

*Propylene Dibromide*, $C_3H_6Br_2$, is a liquid similar to ethylene dibromide, boiling at 141°·6, and having at 17° a specific gravity of 1·9463. It is not only obtained from propylene and bromine, but also when primary or secondary propyl bromide is heated with bromine.[7] When brought in contact with acetic acid and zinc, propylene is rapidly evolved, whilst the dichloride under the same conditions is not attacked (Linnemann). The alcoholic solution is also decomposed by zinc.[8]

*Propylene Iodhydrin*, $C_3H_6I(OH)$, is formed by the combination of propylene oxide and hydriodic acid. It is a liquid which can be distilled under a diminished pressure, but is very easily decomposed (Markownikoff).

[1] Oser, *Bull. Soc. Chim.* 1860, 235.
[2] Markownikoff, *Ann. Chem. Pharm.* cliii. 251.
[3] *Ib.* and *Compt. Rend.* lxxxi. 686, 728, 776.
[4] Schorlemmer, *Proc. Roy. Soc.* xvii. 372.
[5] Friedel and Silva, *Bull. Soc. Chim.* xvi. 3.
[6] Linnemann, *Ann. Chem. Pharm.* clxi. 62.
[7] Linnemann, *ib.* cxxxvi. 51 ; clxi. 41.
[8] Sabanejew, *Ber Deutsch. Chem. Ges.* ix. 1810.

*Propylene Di-iodide*, $C_3H_6I_2$, is formed by the union of iodine with propylene in the sunlight. It is an oily liquid having a specific gravity of 2·49, and is easily decomposed on exposure to light, or on heating, with liberation of iodine (Berthelot and de Luca).

*Propylene Nitrate*, $C_3H_6(NO_3)_2$, is a heavy colourless oily liquid, obtained by adding propylene oxide to cold concentrated nitric acid.[1]

542 *Propylene Diamine*, $C_3H_6(NH_2)_2$, is formed when propylene dibromide is heated for 3 to 4 days to 100° with alcoholic ammonia. The product of the reaction is treated with caustic potash and then warmed with water until the alcohol and excess of ammonia have been volatilized. On distillation the hydrate, $2\,C_3H_6(NH_2)_2+H_2O$, passes over as an oily liquid boiling pretty constantly at 120°, but in the state of vapour this body undergoes dissociation as is shown by its vapour density. In order to obtain the anhydrous base, the hydrate must be repeatedly rectified over sodium. It is an oily liquid boiling at 119°—120°, and having a specific gravity at 15° of 0·878. Exposed to moist air it absorbs water with such avidity, that a glass rod moistened with the substance becomes surrounded by a thick cloud, and the remaining portion solidifies by combining with the atmospheric carbon dioxide to form a crystalline mass.

The hydrochloride, $C_3H_6(NH_3Cl)_2$, is also readily soluble in water, crystallizing in long white needles. It forms a platinochloride, tolerably soluble in water, crystallizing in four-sided tablets.[2]

## TRIMETHYLENE COMPOUNDS.

543 These bodies, which have also been termed the primary propylene compounds, contain the radical trimethylene $-CH_2-CH_2-CH_2-$, a body not known in the free state. The point of departure for these compounds is trimethylene dibromide, a body which, together with propylene dibromide, was first obtained by Geromont, by acting with hydrobromic acid on allyl bromide, the following reactions taking place :[3]

[1] Henry, *Ber. Deutsch. Chem. Ges.* iv. 602. [2] Hofmann, *ib.* vi. 308.
[3] *Ann. Chem. Pharm.* clviii. 369 ; see also Reboul, *Comptes Rendus*, lxxiv. 613.

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2Br \end{array} \qquad HBr \quad = \quad \begin{array}{l} CH_2Br \\ | \\ CH_2 \\ | \\ CH_2Br. \end{array}$$

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2Br \end{array} \quad + \quad HBr \quad = \quad \begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_2Br. \end{array}$$

Under certain circumstances, which will be afterwards detailed, only the first reaction takes place, so that the preparation of pure trimethylene compounds does not offer any difficulty.

*Trimethylene Alcohol*, or *Primary Propylene Glycol*, $C_3H_6(OH)_2$. When the bromide together with potassium acetate and acetic acid is heated to 100°, *trimethylene diacetate*, $C_3H_6(OC_2H_3O)_2$, is formed, a body boiling between 209° and 210°, and this yields the glycol on saponification with caustic baryta.[1] It is a very thick sweet-tasting liquid boiling at 216°, having at 19° a specific gravity of 1·053, and being miscible in every proportion with water and alcohol.

*Trimethylene Oxide*, $CH_2\begin{array}{l}\diagup CH_2 \diagdown \\ \diagdown CH_2 \diagup\end{array}O$, is formed by the action of solid caustic potash on the chlorhydrin. It is a very mobile liquid boiling at 50°, possesses a pungent taste, and is soluble in water.

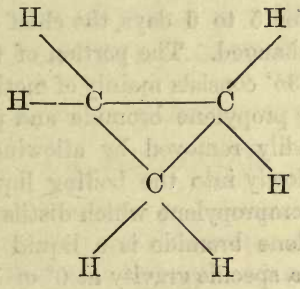
*Trimethylene Chlorhydrin*, $C_3H_6Cl(OH)$, is prepared in a similar way to the corresponding ethylene compound, though by this process some quantity of trimethylene chloride is formed at the same time. These bodies may, however, be readily separated, as the chlorhydrin is easily soluble in water. It is an oily liquid boiling at 160°, and having a specific gravity at 17° of 1·132.

*Trimethylene Chloride*, $C_3H_6Cl_2$, is best prepared by heating the bromide together with mercuric chloride for some time to 160°. It is a pleasantly smelling liquid boiling at 117°, and having at 15° a specific gravity of 1·201.[2]

*Trimethylene Bromide*, $C_3H_6Br_2$, is best obtained by passing hydrobromic acid gas into allyl bromide surrounded by a freezing

[1] Reboul, *Compt. Rend.* lxxix. 169.
[2] Reboul, *Ann. Chim. Phys.* [5], xiv. 460.

mixture at −19° to −16°. When the liquid is saturated it is allowed to stand at a temperature of 35° to 40° in the dark, and this operation repeated until no further absorption of hydrobromic acid takes place.[1] It is a liquid boiling at 163° to 165°, and having a specific gravity at 0° of 2·0177. It differs from the ordinary propylene bromide not only by its high boiling point, but also inasmuch as it is not attacked, in alcoholic solution, by zinc (Sabanejew). When heated with sodium to 220° Reboul and Bourgoin found that ordinary propylene is formed.[2] On the other hand, Freund obtained a gas which combined with difficulty with bromine, with formation of trimethylene bromide, and united with hydriodic acid to form primary propyl iodide.[3] Hence this gas is trimethylene, which, if it contain no free combining units, possesses the following constitution :—



*Methylene Di-iodide*, $C_3H_6I_2$, is obtained by heating the glycol with hydriodic acid. It boils at about 227°, with partial decomposition, but may be distilled at low pressures without undergoing change (Freund).

## DIMETHYL-METHYLENE COMPOUNDS.

544 The starting-point of these is the oxide, a body already described as common acetone, or dimethyl ketone (Part I. p. 568).

*Dimethyl-methylene Chloride*, $(CH_3)_2CCl_2$, was first prepared by Friedel, who termed it methyl chloracetol, by acting with phosphorus pentachloride on acetone :[4]

$$CH_3.CO.CH_3 + PCl_5 = CH_3.CCl_2.CH_3 + POCl_3.$$

[1] Erlenmeyer, *Ann. Chem. Pharm.* cxcvii. 180.
[2] *Bull. Soc. Chim.* xxviii. 54.
[3] *Monatsh. Chem.* ii. 642.
[4] *Ann. Chem. Pharm.* cxii. 236.

In order to prepare this body, acetone is allowed to drop slowly on to well-cooled phosphorus pentachloride, and the dichloride separated from some monochlorpropylene, also produced, by fractional distillation.[1]

The same compound is also formed together with propylene chloride by the action of chlorine on isopropyl chloride.[2] It is a colourless liquid boiling at 69°·7, and having a specific gravity at 16° of 1·1827.[3]

*Dimethyl-methylene Bromide* $(CH_3)_2CBr_2$, also termed *methyl bromacetol*, is obtained by the action of phosphorus pentabromide[4] or phosphorus chlorbromide[5] on acetone. It is best prepared from propylene bromide, which, when heated with alcoholic potash yields a mixture of *a*-brompropylene, $CH_3.CH{=}CHBr$, boiling at 60°, and *β*-brompropylene, $CH_3.CBr{=}CH_2$, boiling at 48°. If this mixture then be treated with highly concentrated hydrobromic acid for 5 to 6 days, the chief part of the *a*-compound remains unchanged. The portion of the product boiling between 115° and 135° consists mainly of methyl bromacetol, but also contains some propylene bromide and propidene bromide, which may be readily removed by allowing alcoholic potash solution to drop slowly into the boiling liquid, when they are converted into *a*-brompropylene which distils off.[6]

Dimethyl-methylene bromide is a liquid boiling at 114° to 114°·5, and having a specific gravity at 0° of 1·8149. It is only with difficulty attacked by alcoholic potash, but easily by sodium ethylate, when *β*-brompropylene is formed, a body which again combines in the cold with hydrobromic acid to form methyl bromacetol. If the latter substance or the chloride be heated with sodium, propylene is formed.

## THE PROPIDENE COMPOUNDS.

545 *Propidene Chloride*, $CH_3.CH_2.CHCl_2$, is formed by the action of phosphorus pentachloride on propionaldehyde. It is a liquid possessing an alliaceous smell and boiling at 85° to 87°, and having at 10° a specific gravity of 1·143 (Reboul).

[1] Friedel and Ladenburg, *Ann. Chem. Pharm.* cxlii. 315.
[2] Friedel and Silva, *Compt. Rend.* lxxiii. 1379.
[3] Linnemann, *Ann. Chem. Pharm.* clxi. 67.
[4] Linnemann, *ib.* cxxxviii. 125.
[5] Friedel and Ladenburg, *Zeitsch. Chem.* 1868, 48.
[6] Reboul, *Ann. Chim. Phys.* [5], xiv. 453.

*Propidene Bromide*, $CH_3.CH_2.CHBr_2$. *a*-Brompropylene combines slowly with hydrobromic acid, with formation of propylene bromide and propidene bromide. This latter is a liquid boiling at about 130°.

The chlorides and bromides which have now been described clearly show the influence which the position of the halogen in the molecule exerts on the boiling point.

Trimethylene Chloride.
$CH_2Cl.CH_2.CH_2Cl$.
117°.

Propylene Chloride.
$CH_3.CHCl.CH_2Cl$.
96°·8.

Propidene Chloride.
$CH_3.CH_2.CHCl_2$
86°.

Diemethyl Methylene Chloride.
$CH_3.CCl_2.CH_3$
69°·7.

## THE LACTYL COMPOUNDS.

### Lactic Acid, or *a*-Oxypropionic Acid,

$CH_3.CH(OH)CO_2H$.

546 This acid was discovered by Scheele in 1780 in sour milk, and was termed by him *acidum lactis s. galacticum.* At first Scheele believed that this substance most closely resembled acetic acid, but afterwards, having discovered malic acid, he came to the conclusion that the acid from sour milk more nearly resembled this fruit acid. Up to the year 1804 Scheele's acid was believed to be a distinct compound, but in that year Bouillon-Lagrange, and in 1806 Fourçroy and Vauquelin, put forward the notion that it is merely acetic acid containing some animal matter. This view was held by many chemists and was made the subject of many varying statements. Berzelius especially, who in 1808 discovered this acid in the juice of flesh, held at different times views respecting the identity of this acid which were antagonistic to one another. It was by the analyses of Liebig and Mitscherlich in 1832 that the individuality of lactic acid was first established, Pelouze and Gay-Lussac arriving at the same result in the following year. The acid found by Bracconnot at Nancy to be contained in sour tan-liquor and in the acid runnings of the starch-makers and similar liquids, and to which he gave the name of *nanceic acid*, was shown by A. Vogel in 1818 to be lactic acid.

Liebig then proved, in 1847, that the lactic acid obtained from flesh differed from ordinary lactic acid, and from this time up to the present, lactic acid has been investigated by many chemists. These researches have tended greatly to the development of theoretical views, as well as to the enlargement of our ideas concerning the theory of types, and that of the linking of atoms. The molecular weight of lactic acid was taken to be double of that which is now adopted, until Wurtz showed that it is formed by the oxidation of propylene glycol in contact with air and platinum black.[1] That the acid is oxypropionic acid was proved by Kolbe, who first ascertained that lactyl chloride, $C_3H_4OCl_2$, obtained by Wurtz by the action of phosphorus pentachloride on calcium lactate, is identical with chlorpropionyl chloride,[2] and this view was confirmed by Ulrich, who found that *a*-chlorpropionic acid when heated with alkalis passes into lactic acid.[3] The same holds good for *a*-brompropionic acid.[4]

Lactic acid was first obtainted synthetically by Strecker, who acted with hydrocyanic acid on aldehyde-ammonia, obtaining a compound which he termed alanin. This substance is amidopropionic acid, and it is transformed, in aqueous solution, into lactic acid by means of nitrogen trioxide.[5] A more ready method of obtaining the body by synthesis is to allow a mixture of aldehyde, hydrocyanic acid, and hydrochloric acid, to stand as long as sal-ammoniac separates out.[6] In this case, the two first of these unite together to form oxypropionitril, a body which will be described further on, and this is converted by the hydrochloric acid into lactic acid:

$$CH_3.CH(OH).CN + 2H_2O + HCl = CH_3.CH(OH).CO_2H + NH_4Cl.$$

As lactic acid is produced from aldehyde or ethidene oxide, it has been termed *ethidene lactic acid*, to distinguish it from its isomerides. It is easily formed by a peculiar fermentation which the various sugars undergo, and hence it has been termed *fermentation lactic acid*. It also occurs in opium, and to this the name of thebolactic acid was given, as it was formerly believed to be a distinct compound, but it is, in fact, identical

[1] *Comptes Rendus*, xlv. 306; xlvi. 12 8; *Ann. Chem. Pharm.* cv. 202; cvii. 193. [2] *Ib.* cix. 257. [3] *Ib.* 268.
[4] Friedel and Machuca, *ib.* cxx. 285.
[5] Strecker, *ib.* lxxv. 27 and 42. [6] Wislicenus, *ib.* cxxviii. 22.

with *a*-oxypropionic acid.[1] This is also the case with the lactic acid produced in certain diseases, as in dyspepsia, where it occurs in the gastric juice,[2] for healthy gastric juice does not, as was formerly supposed, contain this acid.[3] It is also found in *sauerkraut* (Liebig) and in the juice of many other vegetables which have turned sour.

547 *Preparation by Fermentation.* In order to prepare it, the method described for obtaining butyric acid from sugar is used (Part I. p. 591), the fermentation being stopped when the mass has become solid from the formation of calcium lactate. This salt is then decomposed by sulphuric acid, and the filtrate treated with zinc carbonate, when zinc lactate is formed.[4] A simpler plan is to form this salt at once by adding two kilos. of zinc-white instead of chalk. After two or three weeks a magma of zinc lactate is formed, which is purified by recrystallization. It is then dissolved in boiling water and precipitated by sulphuretted hydrogen.[5] The filtrate is concentrated on a water-bath, until mannite, deposited together with the zinc salt, separates out, forming a pasty mass. This is then dissolved in the smallest possible quantity of water, and the lactic acid removed by shaking up with ether.

According to Pasteur, the lactic acid ferment consists of ovoid-cells (*Penicillium glaucum*) usually floating on the surface of the fermenting liquid in the form of a thin scum. This ferment sets up the lactic fermentation in solution of the various kinds of sugar, especially of the glucoses, when kept neutral. Access of air is necessary as well as nitrogenous food, such as hay infusion, &c. The pure ferment forms lactic acid only, without by-products, and it even converts alcohol in presence of infusion into lactic acid.[6] Lactic acid is also formed together with other products when grape-sugar, cane-sugar, or milk-sugar is heated with caustic soda.[7]

548 When a solution of lactic acid is evaporated on a water-bath, a syrupy, inodorous, strongly acid liquid remains behind. This is, however, not the pure acid, but always contains water; and on continued evaporation lactic anhydride is formed. This

[1] Buchanan, *Ber. Deutsch. Chem. Ges.* iii. 182.
[2] Heintz, *Jahresb.* 1849, 525.
[3] Maly, *Ann. Chem. Pharm.* clxxiii. 244; Rabuteau, *Compt. Rend.* lxxx. 61.
[4] Bensch, *Ann. Chem. Pharm.* clxi. 175.
[5] Lautemann, *ib.* cxiii. 142.
[6] Boutroux, *Compt. Rend.* lxxxvi. 605.
[7] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* iv. 346.

formation of lactic anhydride also occurs when the solution is allowed to evaporate at the ordinary temperature in air which is kept dry, and when all the water is evaporated a formation of lactide takes place.[1] The following table gives the composition of some of the preparations thus obtained.

No. 1. A thin syrup purified, as above, with ether, and the residue evaporated in aqueous solution.

No. 2. A syrup obtained after the same acid has dried for four months over sulphuric acid.

No. 3. The same after thirteen months; a thick syrup insoluble in water.

No. 4. The same after sixteen months; a treacly syrup.

No. 5. After eighteen months; a thick gummy mass.

| | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Water, $H_2O$ . . | 15·64 | 4·07 | — | — | — |
| Lactic Acid, $C_3H_6O_3$ | 58·80 | 22·43 | — | — | — |
| Lactic Anhydride, $C_6H_{10}O_5$ . . . | 25·56 | 73·50 | 97·85 | 71·41 | 60·77 |
| Lactide, $C_6H_8O_4$ . | — | — | 2·06 | 28·69 | 39·50 |
| | 100·00 | 100·00 | 99·91 | 100·10 | 100·27 |

Pure anhydrous lactic acid has, therefore, not yet been obtained.

When a galvanic current is passed through a concentrated solution of potassium lactate, the lactic acid decomposes into carbon dioxide and aldehyde.[2] When the acid is heated with dilute sulphuric acid to 130° it is decomposed into aldehyde and formic acid.[3] Aqueous chromic acid solution acts in a similar way, but the products which are formed undergo partial oxidation into acetic acid, carbon dioxide, and water.[4] Nitric acid oxidizes it to water, carbon dioxide, and oxalic acid.[5] Lactic acid is used in medicine.

## The Lactates.

549 The lactates of the alkali metals are almost all uncrystallizable and very deliquescent. They are soluble in alcohol, and are precipitated from an alcoholic solution by ether. They form

[1] Wislicenus, *Ann. Chem. Pharm.* clxiv. 181. [2] Kolbe, *ib.* cxiii. 244.
[3] Erlenmeyer, *Zeitsch. Chem.* 1868, 343.
[4] Dossios, *Jahresb.* 1866, 384; Chapman and Smith, *Journ. Chem. Soc.* [2], v. 173.
[5] Gay-Lussac and Pelouze, *Ann. Chem. Pharm.* vii. 40; Debus, *ib.* cxxvi. 133.

double salts with the lactates of various other metals, some of which crystallize well.

*Sodium Lactate*, $C_3H_5O_3Na$. If the nearly anhydrous salt be allowed to remain for some months in a vacuum it is converted into a solid mass consisting of long, extremely fine, hair-like crystals. When heated to 130°—150° it melts, and dissolves sodium with evolution of hydrogen when the so-called *basic sodium lactate*, $CH_3.CH(ONa).CO_2Na$, is formed. The mass then becomes syrupy, so that the conversion of the normal salt into the basic one is not perfect. Water decomposes this latter compound, in a similar way to sodium ethylate, into the normal salt and caustic soda (Wislicenus).

*Calcium Lactate*, $(C_3H_5O_3)_2Ca + 5H_2O$, forms white opaque, warty, or granular masses, consisting of microscopic rhombic needles. They dissolve in 9·5 parts of cold water, and are much more readily soluble in hot water. If the solution be allowed to evaporate, the salt separates out in light cauliflower-like masses, which cover the sides of the vessel. On heating, it readily loses its water of crystallization, and at 250°—275°, parts with one molecule of water, *calcium dilactate*, $(CH_3CH)_2O(CO_2)_2Ca$, being produced. This forms a tumified mass. Absolute alcohol dissolves out of this some unaltered calcium lactate, the new compound remaining behind as a difficultly soluble residue. The corresponding free acid is not known. The normal salt combines with lactic acid to form the so-called *acid calcium lactate*, crystallizing in fibrous masses resembling wavellite.

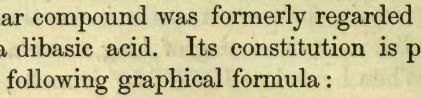
*Zinc Lactate*, $(C_3H_5O_3)_2Zn + 3H_2O$, is the most characteristic salt of this acid. It separates from hot saturated solutions in crusts consisting of monoclinic prisms, which dissolve in about 60 parts of cold, and in 6 parts of boiling water; it is almost insoluble in absolute alcohol. It is used in medicine.

*Ferrous Lactate*, $(C_3H_5O_3)_2Fe + 3H_2O$, crystallizes in light yellow needles, which dissolve in 48 parts of water at 10°, and in 12 parts of boiling water. It is employed in medicine as a mild preparation of iron, and is prepared either by dissolving iron filings in hot lactic acid, or by decomposition of calcium lactate with ferrous sulphate. It is also produced when milk sugar is allowed to ferment in presence of iron filings.[1]

In addition to these lactates, many others are known. These have been chiefly investigated by Engelhardt and Madrell,[2]

[1] Wöhler, *Ann. Chem. Pharm.* xlviii. 149.
[2] *Ib.* lxiii. 88.

and by Brüning.[1] Of these, *stannous lactate*, $(C_3H_4O_3)_2Sn_2$, may be mentioned. It is obtained as a crystalline precipitate by adding sodium lactate to stannous chloride. The existence of this singular compound was formerly regarded as proof that lactic acid is a dibasic acid. Its constitution is probably represented by the following graphical formula:



## THE ETHEREAL SALTS OF LACTIC ACID.

550 *Ethyl Lactate*, $C_3H_5O_3(C_2H_5)$, was first prepared by Strecker by distilling a mixture of calcium lactate with calcium ethyl sulphate.[2] It is best prepared by passing the vapour of absolute alcohol into lactic acid heated to 170°—180°.[3] It is a peculiarly smelling liquid, boiling at 154°·5, and having at 0° a specific gravity of 1·0546.[4] It is miscible with water, but then decomposes quickly into ethyl alcohol and lactic acid.

*Methyl Lactate*, $C_3H_5O_3(CH_3)$, boils at 144°·8, and has at 0° a specific gravity of 1·0898 (Schreiner).

*Ethyl Lactic Acid*, $CH_3CH(OC_2H_5)CO_2H$. In order to prepare this compound, which is also known as *Ethoxypropionic Acid*, the ethyl ether is employed, and this is obtained by acting with sodium ethylate on the ethyl ether of *a*-chlorpropionic acid.[5] By boiling this with caustic potash the potassium salt is obtained, and in order to remove the free caustic potash it is neutralized with dilute sulphuric acid and evaporated down. Potassium ethyl lactate is extracted from the residue by alcohol, the solution evaporated, and the salt distilled with dilute sulphuric acid.

Sodium ethyl lactate is also formed, together with methylene iodide and other products, when iodoform is heated with sodium ethylate in alcoholic solution. The acid thus obtained was described by Butlerow as *valerolactic acid*.[6] The explanation of its formation in this complicated reaction is still wanting.

It is a thick liquid having a strongly acid reaction, and is

[1] *Ann. Chem. Pharm.* civ. 192. [2] *Ib.* xci. 355.
[3] Wislicenus, *ib.* cxxv. 58.
[4] Schreiner, *Ann. Chem. Pharm.* cxcvii. 12.
[5] Wurtz, *Ann. Chim. Phys.* [3], lix. 171.
[6] *Ann. Chem. Pharm.* cxiv. 204; cxviii. 325.

easily soluble in water, alcohol, and ether, and boils with slight decomposition at 195°—198°.

Its most characteristic is *silver ethyl lactate*, $C_3H_4(OC_2H_5)CO_2Ag$. which crystallizes from hot water in silky needles, and is also tolerably soluble in cold water.

*Ethyl Etholactate*, $CH_3.CH(OC_2H_5)CO_2C_2H_5$, is not only produced in the above reaction, but is formed when ethyl lactate is treated with potassium and then with ethyl iodide.[1] It is a mobile, pleasantly smelling liquid, boiling at 155°, and having at 0° a specific gravity of 0·9498 (Schreiner).

*Nitroxylactic Acid*, $CH_3CH(NO_3)CO_2H$. This nitrate, which is usually called *nitrolactic acid*, is obtained by dissolving lactic acid in a mixture of concentrated nitric and sulphuric acids and subsequent precipitation with water, when it is thrown down as a thick oil, easily soluble in ether, which decomposes with formation of oxalic acid, hydrocyanic acid, and water.[2]

$$CH_3.CH(NO_3)CO.OH = CO(OH).CO.OH + CHN + H_2O.$$

Its ethyl ether is formed in a similar way to the acid. It is a mobile liquid possessing a sweet and pungent taste, and smelling like ethyl nitrate. It boils at 178°, and at 13° has a specific gravity of 1·1534.

*Acetolactic Acid*, $CH_3.CH(OC_2H_3O)CO_2H$. The ethyl ether of this acid is formed by the action of acetyl chloride on ethyl acetate, and is a pleasantly smelling liquid, boiling at 177°, and having a specific gravity of 1·0458 at 17°. When heated with twice its volume of water for 2 to 3 hours to 150° the free acid is formed. This is a thick acid syrup, and is easily decomposed by alkalis into an acetate and a lactate.[3]

*Lactyl Ethyl Lactate*, $CH_3CH(OC_3H_5O_2)CO_2(C_2H_5)$, is formed when ethyl chlorpropionate is heated to 100° with a solution of potassium lactate. It is an oily liquid, boiling at 235°, and having at 0° a specific gravity of 1·134.[4]

551 *Lactolactic Acid*, $CH_3.CH(OH)CO_2.CH(CH_3)CO_2H$. This compound, which is usually called *lactic anhydride*, was first obtained by Pelouze by heating lactic acid to 130°—140°.[5] It is also formed, as has been stated, when a solution of lactic acid is allowed to evaporate at the ordinary temperature (p. 135), or

[1] Friedel and Wurtz, *Ann. Chim. Phys.* [3], lxiii. 117.
[2] Henry, *Ber. Deutsch. Chem. Ges.* iii. 532 ; xii. 1837.
[3] Wislicenus, *Ann. Chem. Pharm.* cxxv. 60.
[4] Wurtz and Friedel, *Compt. Rend.* lii. 1067.
[5] *Ann. Chem. Pharm.* lxiii. 112.

when potassium lactate is heated to 100°—120° with *a*-brom-propionic acid :[1]

$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO.OH \end{array} + \begin{array}{l} KO.CO \\ | \\ CH.OH \\ | \\ CH_3 \end{array} = \begin{array}{l} CH_3 \\ | \\ CH.O.CO \\ | \quad\quad | \\ CO.OH\ CH.OH \\ \quad\quad\quad | \\ \quad\quad\quad CH_3. \end{array} + KBr.$$

It is a light yellow amorphous mass, easily soluble in alcohol and ether, but scarcely soluble in water. It is a monobasic acid, forming salts which are easily converted by assumption of water into a lactate and lactic acid. Alkalis at once convert the anhydride into a lactate. When its ethereal solution is treated with ammonia, ammonium lactate separates out and lactamide remains in solution.[2]

*Lactide*, $CH_3.CH\begin{matrix} O.CO \\ \diagup\quad\diagdown \\ CO.O \end{matrix}CH.CH_3$, is formed when the foregoing compound is disitlled, or when dry air is passed over lactic acid heated to 150°.[3] It is scarcely soluble in water, and crystallizes in monoclinic tables, which melt at 124°·5. At 255° it boils, and yields a vapour having a specific gravity of 4·81.[4] When left in contact with water for some time it is converted into lactic acid, and this conversion takes place quickly in presence of alkalis.

552 *a-Chlorpropionic Acid*, $CH_3.CHCl.CO_2H$, is formed by the action of chlorine on propionic acid or its anhydride. It is, however, best obtained from lactic acid; by the action of phosphorus pentachloride on the calcium salt, Wurtz obtained *a-chlorpropionyl chloride*, $CH_3.CHCl.COCl$, which he termed *lactyl chloride*.[5] This can be best obtained by heating well-dried lactic acid with phosphorus pentachloride in the quantity given in the following equation :

$$C_3H_6O_3 + 2PCl_5 = C_3H_4OCl_2 + 2POCl_3 + 2HCl.$$

the product being heated until no more hydrochloric acid is evolved.[6]

[1] Brüggen, *Zeitsch. Chem.* 1869, 338.
[2] Wislicenus, *Ann. Chem. Pharm.* cxxxiii. 257.
[3] Wislicenus, *ib.* clxvii. 318.
[4] Henry, *Ber. Deutsch. Chem. Ges.* vii. 753.
[5] Wurtz, *Comptes Rendus*, xlvi. 1228 ; *Ann. Chem. Pharm.* cvii. 192.
[6] Brühl, *Ber. Deutsch. Chem. Ges.* ix. 35.

It is a pungent, fuming liquid, which has not yet been obtained in the pure state. It boils above 140° with partial decomposition, and this takes place also when the substance is allowed to stand. Water causes rapid decomposition with formation of chlorpropionic acid, a pungent-smelling, caustic liquid, boiling at 186°, and having a specific gravity at 0° of 1·28. It is miscible with water, and forms a silver salt crystallizing in quadratic prisms, much more soluble than silver proprionate. When the acid is treated with zinc and hydrochloric acid it is reduced to propionic acid.

*a-Ethyl Chlorpropionate*, $CH_3.CHCl.CO_2(C_2H_5)$, is easily obtained by the action of the chloride on absolute alcohol. It is an aromatic smelling liquid, boiling at 146°, and having at 0° a specific gravity of 1·079.

*a-Brompropionic Acid*, $CH_3CHBr.CO_2H$, is formed by heating equal molecules of bromine and propionic acid to 130°,[1] and also by heating lactic acid with concentrated hydrobromic acid to 100°.[2] It is a liquid boiling at 205°·5, and solidifying at —17° to a striated mass. When boiled with twenty-five times its weight of water for thirty hours it is converted into lactic acid.[3]

*a-Ethyl Brompropionate*, $C_3H_4BrCO_2(C_2H_5)$, is formed by the action of phosphorus pentabromide on ethyl lactate, and is a liquid boiling with partial decomposition at 159°—160°.

*a-Iodpropionic Acid*, $CH_3.CHI.CO_2H$, was obtained by Wichelhaus by acting with phosphorus diiodide on syrupy lactic acid. It is an oily liquid, slightly soluble in water, which has not been more closely investigated.[4]

## SULPHUR COMPOUNDS OF LACTYL.

553 *Thiolactic Acid*, $CH_3.CH(SH).CO_2H$. The potassium salt of thiolactic acid is obtained by boiling one part of ethyl chlorpropionate with two parts of potassium hydrosulphide for two days.[5] The solution is neutralized with hydrochloric acid and precipitated with lead acetate with addition of ammonia. The washed lead salt is then decomposed by sulphuretted hydrogen, and the acid extracted from the filtrate by ether and converted

[1] Friedel and Machuca, *Ann. Chem. Pharm.* cxx. 286.
[2] Kekulé, *ib.* cxxx. 16.
[3] Fittig and Thomson, *ib.* cc. 79.
[4] *Ib.* cxliv. 352.
[5] Schacht, *ib.* cxxix. 1.

a second time into the lead salt for further purification. The acid crystallizes from water in hard distinct needles which melt at 142°.[1]

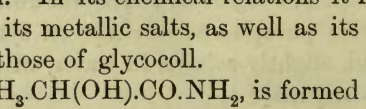
*Thio-dilactic Acid*, $S(CH)_2(CH_3)_2(CO_2H)_2$, is formed together with the preceding compound as an oily liquid soluble in water.

## AMIDO-COMPOUNDS OF LACTYL.

554 *α-Amidopropionic Acid*, $CH_3CH(NH_2).CO_2H$, was first prepared by Strecker by heating a mixture of aldehyde-ammonia, formic acid, and hydrocyanic acid together, and termed by him *Alanin*.[2] In this case the corresponding nitril, a body to be hereafter described, is first formed. Alanin is also formed when *α*-ethyl chlorpropionate is heated with ammonia,[3] or when brom-propionic acid is treated in the same way with alcoholic ammonia.[4] It crystallizes in needles or monoclinic prisms which possess a sweet taste, and dissolve in 4·6 parts of water at 17°. They are very difficultly soluble in strong alcohol. Alanin, when carefully heated, may be sublimed, but if quickly heated it decomposes chiefly into carbon dioxide and ethylamine. As it has a perfectly neutral reaction, it must be regarded like glycocoll as a saline compound. In its chemical relations it resembles amido-acetic acid, and its metallic salts, as well as its compounds with acid, resemble those of glycocoll.

*Lactamide*, $CH_3.CH(OH).CO.NH_2$, is formed by the action of ammonia on ethyl lactate,[5] lactide,[6] or lactic anhydride.[7] It forms radiated crystals, which are soluble in water and alcohol, but difficultly soluble in ether. These melt at 74°, and, when more strongly heated, volatilize without decomposition.

*Lactimide*, $C_3H_5ON$, is formed when alanin is heated to 180°—200° in a stream of hydrochloric acid:



[1] Böttinger, *Ann. Chem. Pharm.* cxcvi. 103
[2] *Ib.* lxxv. 29.
[3] Kolbe, *ib.* cxiii. 220.
[4] Kekulé, *ib.* cxxx. 18.
[5] Brüning, *ib.* civ. 197.
[6] Wurtz and Friedel, *Ann. Chim. Phys.* [3], lxiii. 108.
[7] Wislicenus, *Ann. Chem. Pharm.* cxxxiii. 259.

It is soluble in water, crystallizes in needles or tablets which melt at 275°, and sublimes when strongly heated. It acts as an indifferent body towards both acids and bases.[1]

Many other compounds belonging to this group are known, which closely resemble the corresponding compounds in the glycolyl series.

## CARBAMIDE AND GUANIDINE COMPOUNDS OF LACTYL.

555 *Lactyl Urea*, $CO\begin{<}\begin{matrix}NH.CH.CH_3\\ |\\ NH.CO\end{matrix}\end{>}$, is formed when a mixture of equal molecules of aldehyde-ammonia, potassium cyanide, and potassium cyanate are evaporated with hydrochloric acid. From the product of this reaction the above compound can be separated by a mixture of alcohol and ether. It forms warty concretions or transparent crystals, which contain one molecule of water, which they readily lose. The anhydrous compound melts at 145°.[2]

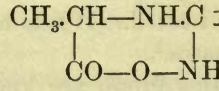
*Lacturamic Acid*, $CO\begin{<}\begin{matrix}NH—CH.CH_2\\ |\\ NH_2\ \ CO.OH\end{matrix}\end{>}$, is formed when the preceding compound is warmed with baryta water, as well as when potassium cyanate is allowed to act on an aqueous solution of alanine sulphate.

Lacturamic acid crystallizes from dilute alcohol in indistinct forms. It is difficultly soluble in water, melts at 155° with decomposition, and forms salts, some of which are amorphous, whilst others crystallize well.[3]

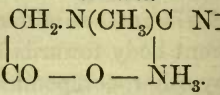
*Alacreatine* or *Guanidopropionic Acid*, $C_4H_9N_3O_2$. This compound, isomeric with creatine, is formed when a concentrated solution of alanin and cyanamide is treated with some ammonia and the whole mixture allowed to stand. It is more easily soluble in water than creatine, and crystallizes in colourless prisms. The isomerism of the two compounds is explained by the following formulæ :

[1] Preu, *Ann. Chem. Pharm.* cxxxiv. 372.
[2] Urech, *Ber. Deutsch. Chem. Ges.* vi. 1113.
[3] Urech, *Ann. Chem. Pharm.* clxv. 99.

Alacreatine.



Creatine.

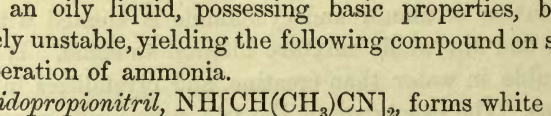


*Alacreatinine* or *Lactyl-Guanidine*, $C_4H_7N_3O + H_2O$, is formed when the foregoing compound is heated to 170°—180°. It crystallizes from water in long needles which easily lose their water of crystallization. From alcohol it crystallizes in small anhydrous rhombohedrons. Like creatinine it is a strong base and forms corresponding compounds.[1]

## LACTYL NITRILS.

556 *Lactyl Nitril* or *a-Oxypropionitril*, $CH_3.CH(OH).CN$, is formed when equal volumes of aldehyde and anhydrous hydrocyanic acid are allowed to stand for some days at 20°—30°. It is a liquid having a sharp bitter taste, and in smell resembling its constituents, into which it is partially decomposed on heating. The chief portion, however, distils over at 182°—184°. Caustic potash decomposes it with formation of potassium cyanide and aldehyde-resin and hydrochloric acid acts violently upon it with formation of lactic acid.[2]

*Amidopropionitril*, $CH_3.CH(NH_2)CN$, is obtained when an aqueous solution of equal molecules of hydrocyanic acid and aldehyde ammonia is acidified with sulphuric acid and the mixture allowed to stand :

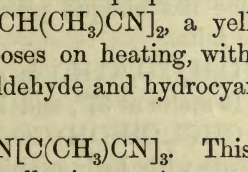


It is an oily liquid, possessing basic properties, but it is extremely unstable, yielding the following compound on standing, with liberation of ammonia.

*a-Imidopropionitril*, $NH[CH(CH_3)CN]_2$, forms white needles, and separates out, on the slow evaporation of its ethereal solution, in monoclinic crystals which melt at 68°. It is a weak base, and

[1] Baumann, *Ann. Chem. Pharm.* clxvii. 77.
[2] Simpson and Gautier, *Bull. Soc. Chim.* [2], viii. 277.

when boiled with dilute hydrochloric acid or baryta water, yields *Imidopropionic acid,* or *Dilactamidic acid,* $NH[CH(CH_3)CO_2H]_2$, which forms a deliquescent amorphous mass. This acid is monobasic, and probably has the following constitution :



Nitrous acid converts imidopropionitril into *nitroso-a-imido-propionitril,* $N(NO)[CH(CH_3)CN]_2$, a yellow oil, heavier than water, which decomposes on heating, with formation of brown vapours, a smell of aldehyde and hydrocyanic acid being at the same time observed.[1]

*Hydrocyanaldine,* $N[C(CH_3)CN]_3$. This body was first obtained by Strecker by allowing a mixture of aldehyde-ammonia, hydrocyanic acid and hydrochloric acid, to stand.[2] It is doubtless a product of decomposition of amidopropionitril, which, under these circumstances, is first formed. If the above mixture be allowed to stand for four to five weeks, crystals are deposited which may be separated from the amido- and imido-propionitrils, which are formed at the same time. It is difficultly soluble in water and somewhat more readily soluble in alcohol and ether. In presence of imidopropionitril it dissolves in the latter more readily, and separates on slow evaporation in large monoclinic prisms which melt at 115°, and can be sublimed by careful heating without decomposition (Erlenmeyer and Passavant).

If the above mixture be allowed to stand for a few months, or if it be heated on the water-bath, *parahydrocyanaldine* is formed. This substance is difficultly soluble in water and alcohol, and is insoluble in ether. It separates from a solution in acetone in rhombic crystals, which melt at 230°—232°. It has the same composition as hydrocyanaldine, with which it is no doubt polymeric, the cyanogen being converted into dicyanogen and tricyanogen (Erlenmeyer and Passavant).

[1] Erlenmeyer and Passavant, *Ann. Chem. Pharm.* cc. 120.
[2] *Ib.* xci. 349.

## SUBSTITUTION PRODUCTS OF LACTIC ACID.

**557** These bodies have not been obtained directly from lactic acid, but may be prepared by other reactions.

*Monochlorlactic Acid*, $CH_2Cl.CH(OH).CO_2H$. The nitril of this body is obtained by the union of monochloraldehyde with hydrocyanic acid, and is easily decomposed by hydrochloric acid. Chlorlactic acid is very easily soluble in water, alcohol, and ether, and crystallizes in fine flat oblique prisms which melt at 71°. It forms crystallizable salts.

*Ethyl Chlorlactate*, $C_3H_4ClO_3(C_2H_5)$, is a colourless crystalline saponaceous mass. It melts at 37°, and boils at 205°.[1]

*Dichlorlactic Acid*, $CHCl_2.CH(OH).CO_2H$, is obtained by the union of dichloraldehyde with hydrocyanic acid and decomposition of the resulting nitril. It forms deliquescent prisms which melt at 76°·5—77°.[2]

*Trichlorlactic Acid*, $CCl_3.CH(OH).CO_2H$. The nitril of this body is formed by the union of hydrocyanic acid with chloral. It is easily soluble in water and crystallizes in tablets which melt at 61°, and boil at 215°—220°, with partial decomposition. When heated with concentrated hydrochloric acid, trichlorlactic acid is formed, and this may be separated by ether from the sal-ammoniac formed at the same time. On evaporating the solution, the acid remains behind as a syrup, which solidifies in a vacuum to a crystalline mass consisting of thin prisms which melt at 105°—110°. Weak bases easily decompose it into chloral and formic acid, whilst alkalis naturally yield chloroform. Hence, in preparing its salts, all heating must be avoided.[3]

*Ethyl Trichlorlactate*, $CCl_3.CH(OH).CO_2(C_2H_5)$, is formed when hydrochloric acid is passed into an alcoholic solution of trichlorlactic acid. It crystallizes in tablets melting at 66°—67°, boils at 233°—237°, and is insoluble in water. On the other hand, it is easily soluble in cold dilute aqueous alkalis, and is precipitated from these solutions on the addition of acids, or even by carbon dioxide. Hence it behaves as a weak acid in accordance with its constitution.[4] The alkaline salts decompose

[1] Frank, *Ann. Chem. Pharm.* ccvi. 338.
[2] Grimaux and Adam, *Ber. Deutsch. Chem. Ges.* x. 903; xiii. 1864.
[3] Pinner and Bischoff, *Ann. Chem. Pharm.* clxxix. 79.
[4] Claisen and Antweiler, *Ber. Deutsch. Chem. Ges.* xiii. 1940.

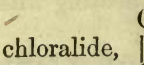
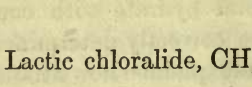
gradually in the cold, and quickly on heating with formation of chloroform, &c.

558 *Chloralide*, $C_5H_2Cl_6O_3$. This peculiar compound was first prepared by Städeler by heating chloral hydrate with concentrated sulphuric acid, and he likewise correctly determined its composition.[1] It, however, remained unexplained how a molecule of a body containing two atoms of carbon can be converted, by such an apparently simple reaction, into another molecule containing five atoms, and hence the formula which Städeler gave was doubted. Kekulé,[2] however, showed that no mistake had been made, and Wallach[3] solved the enigma by showing that on heating chloralide with absolute alcohol to 140°—150°, chloral alcoholate and ethyl trichlorlactate are formed. According to this, chloralide must be looked upon as the trichlorlactic ether of trichlorethidene, and Wallach succeeded in preparing this compound by heating chloral with trichlorlactic acid to 150°:

$$CCl_3CH\begin{matrix}OH\\CO_2H\end{matrix} + COH.CCl_3 = CCl_3CH\begin{matrix}O\\CO_2\end{matrix}CH.CCl_3 + H_2O.$$

Its formation from chloral doubtless takes place in several phases, as it is very probable that the lactide of trichlorlactic acid is formed by separation of chloroform, and this again combines with chloral. In order to prepare chloralide, chloral hydrate is mixed with three times its volume of a mixture of sulphuric acid and disulphuric acid, having a specific gravity of 1·84 to 1·85, and the whole heated until the chloral begins to distil off. The source of heat is then removed and the flask well shaken until the reaction ceases. The operation is repeated until oily drops begin to condense in the neck of the flask, and then it is allowed to cool and frequently shaken. The chloralide which separates out is washed with warm water and crystallized from ether. It forms large pliable monoclinic prisms, melting at 114°—115°, and boiling at 270°—273°. Its vapour has a peculiar smell and a specific gravity of 11·3.[4] Other oxyacids form, like trichlorlactic acid, compounds analogous to chloralide, termed by Wallach *chloralides*, of which the following may be mentioned:

[1] *Ann. Chem. Pharm.* lxi. 101.
[2] *Ib.* cv. 293.
[3] *Ib.* cxciii. 1.
[4] *Ber. Deutsch. Chem. Ges.* viii. 1433.

| | M. P. |
|---|---|
| Glycollic chloralide,  | 41—42° |
| Lactic chloralide,  | 45° |

Bromal also forms a a series of *bromalides* (Wallach).

In addition to the chlorlactic acids, the following substitution products are known :

| | M. P. |
|---|---|
| [1] Monobromlactic acid, $C_3H_5BrO_3$ . . | 89—90° |
| [2] Dibromlactic acid, $C_3H_4Br_2O_3$ . . . | 98° |
| [3] Tribromlactic acid, $C_3H_3Br_3O_3$ . . | 141—143° |
| [4] Moniodlactic acid, $C_3H_5IO_3$ . . . . | 84—85° |

## PARALACTYL COMPOUNDS.

559 *Paralactic Acid,* $CH_3.CH(OH).CO_2H$. It has already been stated that Liebig was the first to show that the acid contained in the juice of flesh is not identical with common lactic acid, and hence it was termed *sarcolactic acid.* The same acid occurs in the bile,[5] as well as in the urine in cases of phosphorus poisoning.[6] Engelhardt [7] and Heintz [8] investigated this subject more accurately, and the latter, who determined the composition of the acid with great care, gave to it the name of *paralactic acid.*

For the purpose of preparing this acid, extract of meat is used. This is dissolved in four parts of warm water, and to the solution double its volume of 90 per cent. alcohol added. The filtrate is evaporated to a thin syrup, and again treated with three to four times its volume of alcohol, again filtered and the filtrate acidified with dilute sulphuric acid, and paralactic acid extracted from the solution by shaking with ether. The residual crude acid remaining on evaporating off the ether is neutralized with lead carbonate, and the filtrate treated with sulphuretted

[1] Melikow, *Ber. Deutsch. Chem. Ges.* xiii. 958.
[2] Linnemann and Penl, *ib.* viii. 1101.
[3] Pinner, *ib.* vii. 1501 ; Wallach, *loc. cit.*
[4] Glinsky, *ib.* vi. 1257.
[5] Strecker, *Ann. Chem. Pharm.* cxxiii. 354.
[6] Schultzen, *Zeitsch. Chem.* 1867, 138.
[7] *Ann. Chem. Pharm.* lxv. 359.
[8] *Pogg. Ann.* lxxv. 391.

hydrogen. The liquid separated from lead sulphide is then heated to boiling, and treated with zinc carbonate, and the solution evaporated until the zinc salt begins to crystallize out, when it is precipitated by alcohol. The salt is then purified by repeated solution in water and precipitation with alcohol, after which it is decomposed by sulphuretted hydrogen.[1]

Paralactic acid can only be distinguished from ordinary (fermentation) lactic acid by the fact that it turns the plane of polarization to the right, whilst the ordinary acid is inactive.[2]

In a dry atmosphere it passes into the anhydride, which is levro-gyratory, and when heated to 150°, it yields common lactide, which combines with water to form the inactive fermentation lactic acid.[3] Like this latter substance, paralactic acid decomposes on heating with dilute sulphuric acid into aldehyde and formic acid, whilst chromic acid oxidizes it to acetic acid and carbon dioxide. Both acids have therefore the same constitution, and hence they are physical isomerides.

The salts of paralactic acid are levro-rotatory, and more easily soluble in water than those of the fermentation-lactic acid.

*Calcium Paralactate*, $2(C_3H_5O_3)_2Ca + 9H_2O$, resembles common calcium lactate, dissolves in 12·4 parts of cold water, and in all proportions in boiling water.

*Zinc Paralactate*, $(C_3H_5O_3)_2Zn + 2H_2O$, crystallizes in needles which melt at 14°—15° in 17·5 parts of water, and are only very slightly soluble in spirit of wine.

*Ethyl Paralactate*, $C_3H_5O_3(C_2H_5)$, corresponds closely to ethyl lactate, but is strongly levro-rotatory.[4]

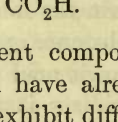
*Amidoparalactamide*, $CH_3.CH(NH_2)CONH_2$, occurs in small quantity in urine. It crystallizes from hot water in small prisms. It forms deliquescent salts with acids, and when heated with baryta water to 150° it decomposes into carbon dioxide, ammonia, and ethylamine. Nitrous acid converts it into paralactic acid.[5]

[1] Wislicenus, *Ann. Chem. Pharm.* clxvii. 302.
[2] Wislicenus, *Ber. Deutsch. Chem. Ges.* ii. 550 and 619.
[3] Strecker, *Ann. Chem. Pharm.* cv. 313; Wislicenus, *ib.* clxvi. 316.
[4] Klimenko, *Journ. Russ. Chem. Ges.* xii. 17.
[5] Baumstark, *Ann. Chem. Pharm.* clxxiii. 342.

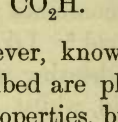
## HYDRACRYL COMPOUNDS.

560 *Hydracrylic Acid,* or *β-Oxypropionic Acid,* $CH_2(OH).CH_2.CO_2H$. According to theory two oxypropionic acids should exist:

α-Oxypropionic Acid.



β-Oxypropionic Acid.



Four different compounds are, however, known. Of these the two which have already been described are physical isomerides. They exhibit different optical properties, but chemically they are identical, and they are distinguished as the *α*-compounds. The two other acids which, from their mode of formation, are termed the *β*-compounds, exhibit totally different chemical relations.

In 1863, Wislicenus prepared one of these acids synthetically by heating ethylene chlorhydrin with potassium cyanide, and boiling the nitril thus obtained with caustic soda. He termed this *ethylene-lactic acid,* and first thought that it was identical with sarcolactic acid. He afterwards found that this latter is a mixture of optically active lactic acid, with a small quantity of ethylene-lactic acid.[1]

The fourth isomeric acid was first prepared by Beilstein by the action of silver oxide and water upon *β*-iodpropionic acid. It was termed by him *hydracrylic acid,* since it decomposes on heating into water and acrylic acid.[2] Its true formula was ascertained by Moldenhauer,[3] and it was investigated more accurately by Heintz[4] as well as by Wislicenus.[5] According to this latter chemist, it is distinguished from ethylene-lactic acid not only by the different properties of its salts, but also by its reaction with hydriodic acid, as on heating it is easily converted back into *β*-iodpropionic acid, whilst this is not the case with ethylene lactic acid.[6]

Linnemann found that when acrylic acid is heated with caustic soda, hydracrylic acid is formed, together with an almost equal

[1] *Ber. Deutsch. Chem. Ges.* ii. 550.
[2] *Ann. Chem. Pharm.* cxxii. 366.
[3] *Ib.* cxxxi. 328.
[4] *Ib.* clvii. 291.
[5] *Ib.* clxvi. 6.
[6] *Ib.* clxvii. 346.

quantity of ethylene-lactic acid.[1] Wislicenus observed that in the preparation of ethylene-lactic acid from its nitril, some hydracrylic acid is always formed, whilst in the preparation of hydracrylic acid from β-iodpropionic acid, a small quantity of ethylene-lactic acid is also produced, but, singularly enough, common lactic acid also occurs.[2]

The latest investigations on this subject are those of Erlenmeyer. He did not find any ethylene-lactic acid in sarcolactic acid. From its nitril, which he was the first to prepare in the pure state, he only obtained hydracrylic acid, together with some acrylic acid, but no ethylene-lactic acid. Moreover he could not obtain this latter body according to the process described by Linnemann, and hence his belief in the existence of ethylene lactic acid has been somewhat shaken.[3] Hence it appears probable that this is only an impure hydracrylic acid, or a mixture of this body with common lactic acid. Further investigation is, however, here needed.

561 In order to prepare hydracrylic acid, freshly precipitated silver oxide is added to a hot solution of β-iodpropionic acid as long as silver oxide is precipitated, the filtrate treated with sulphuretted hydrogen-water, and the filtrate evaporated with zinc carbonate. On slow evaporation, zinc hydracrylate separates out, and this is purified by recrystallization and then decomposed by sulphuretted hydrogen. Hydracrylic acid is also formed when β-iodpropionic acid is boiled in connection with a reversed condenser with twenty-five times its weight of water for sixteen hours.[4]

Hydracrylic acid, like the other lactic acids, consists in the concentrated state of a thick acid syrup, and it decomposes on heating into water and acrylic acid.

*Sodium Hydracrylate*, $C_3H_5O_3Na$, separates out from its solution in nearly absolute alcohol in colourless crystals, which melt at 143°.

*Calcium Hydracrylate*, $(C_3H_5O_3)_2Ca + 2H_2O$, is easily soluble in water, and crystallizes in rhombic prisms.

*Zinc Hydracrylate*, $(C_3H_5O_3)_2Zn + 4H_2O$, is deposited in well-formed triclinic crystals, which dissolve at 16°·5 in 0·89 parts of water. If concentrated solutions of this salt and calcium hydracrylate be mixed, they deposit a characteristic double salt,

[1] *Ber. Deutsch. Chem. Ges.* viii. 1095. [2] *Ib.* 1206
[3] *Ann. Chem. Pharm.* cxci. 261.
[4] Fittig and Thomson, *ib.* cc. 81.

$(C_3H_5O_3)_2Ca + (C_3H_5O_3)_2Zn$, which crystallizes in prisms, and is very slightly soluble in water.

The hydracrylates lose water on heating, and are transformed into the salts of acrylic acid, $C_3H_4O_2$, or diacrylic acid, $C_6H_8O_4$.

562 *β-Chlorpropionic Acid*, $CH_2Cl.CH_2.CO_2H$, is formed by heating acrylic acid with fuming hydrochloric acid to 130°,[1] as well as by boiling iodpropionic acid with chlorine water,[2] and by oxidizing trimethylene chlorhydrin.[3] It is crystalline, easily soluble in water, and melts at 78° to 79°.

*β-Brompropionic Acid*, $CH_2Br.CH_2.CO_2H$, is obtained in an analogous way to the foregoing compound. It is deposited in crystals which melt at 89° to 90°.[4]

*β-Iodpropionic Acid*, $CH_2I.CH_2.CO_2H$. In order to prepare this, 100 grams of phosphorus diiodide are gradually added to 52 cc. of aqueous glyceric acid, having a specific gravity of 1·26.[5] After a short time a violent reaction takes place, which is usually followed by another and less violent one. If this is not the case the reaction must be brought about by heat. The crystalline mass obtained on cooling is then boiled with petroleum spirit or sulphide of carbon.[6] Its formation is represented by the following equation:

$$CH_2(OH).CH(OH).CO_2H + 3HI = CH_2I.CH_2.CO_2H + 2H_2O + I_2.$$

No free iodine is, however, formed, as this acts upon the phosphorus acid which is produced in presence of water to form phosphoric acid and hydriodic acid.

The acid is also formed by heating acrylic acid with hydriodic acid.[7]

β-Iodpropionic acid is difficultly soluble in cold, but easily soluble in hot water, and readily soluble in alcohol and ether. It crystallizes in glistening laminæ which melt at 100°—101°.

*β-Nitropropionic Acid*, $CH_2(NO_2).CH_2.CO_2H$. In order to prepare this substance, silver nitrite is gradually added to a well-cooled aqueous solution of iodpropionic acid, the mixture then acidified with hydrochloric acid and well shaken with ether, and the residue obtained on evaporation crystallized from hot chloroform. Nitropropionic acid forms pearly glistening scales, melting

[1] Linnemann, *Ann. Chem. Pharm.* clxiii. 95.
[2] Richter, *Zeitsch. Chem.* 1868, 451.
[3] Kayser, *Inauguraldiss. München*, 1875.
[4] Linnemann; Richter.
[5] Beilstein, *Ann. Chem. Pharm.* cxx. 226; cxxii. 366.
[6] Erlenmeyer, *ib.* cxci. 284.
[7] Wislicenus, *ib.* clxvi. 2.

at 66°—67°, and easily soluble in water. The salts are very unstable.[1]

*β-Ethyl Nitropropionate,* $CH_2(NO_2).CH_2.CO_2(C_2H_5)$, is obtained by the action of silver nitrite on the ethyl ether of iodpropionic acid. It is a mobile ethereal-smelling liquid, boiling at 161°—165°.

*β-Amidopropionic Acid,* $CH_2(NH_2).CH_2.CO_2H$, is formed by the action of ammonia on iodpropionic acid.[2] It is easily soluble in water, less soluble in alcohol, crystallizes in prisms, and has a sweet taste. On heating it melts and decomposes into acrylic acid and ammonia.

*β-Lactonitril,* $CH_2(OH).CH_2.CN$, is obtained by heating ethylene oxide with hydrocyanic acid under pressure. It is a colourless liquid having a faint sweet smell, and at 0° has a specific gravity of 1·0588. It boils at about 220°, and is miscible with water.

## PYRUVYL COMPOUNDS.

563 *Pyroracemic,* or *Pyruvic Acid,* $CH_3.CO.CO_2H$. This compound, which stands in the same relation to lactic acid as acetone does to isopropyl alcohol, is produced along with many other products in the dry distillation of tartaric acid, $C_4H_6O_6$, and of cream of tartar (acid potassium tartrate). Raymond Lully described the distillation of the latter compound, but the acid product was not examined until the 16th century, when it was described as *spiritus tartari.* Paracelsus, in his tract *De Naturalibus Rebus,* recommends it as a medicine. Various chemists then examined the substance, amongst others Guyton de Morveau, who distinguishing it as a peculiar acid gave to it the name of *acid tartareux empyreumatique,* which name was afterwards changed to the antiphlogistic designation of *acide pyrotartareux.* Fourçroy and Vauquelin in 1800 stated that this acid was merely impure acetic acid. This conclusion was, however, contradicted by V. Rose in 1807, who showed that the product of distillation contained a peculiar acid. At the same time he remarked that a second distinct acid seems to be formed under the same circumstances. This latter was prepared and investigated by Berzelius.

[1] Lewkowitsch, *Journ. Prakt. Chem.* [2], xx. 169.
[2] Heintz, *Ann. Chem. Pharm.* clvi. 36; Mulder, *Ber. Deutsch. Chem. Ges.* ix. 1903.

As, however, this is formed not only in the distillation of tartaric acid, but also in that of its isomeride racemic acid, he termed it pyruvic acid, to distinguish it from pyrotartaric acid.[1] It is also formed by the distillation of glyceric acid.[2]

$$CH_2(OH).CH(OH).CO_2H = CH_3.CO.CO_2H + H_2O.$$

Pyruvic acid has been prepared synthetically by acting with hydrochloric acid on acetyl cyanide, $CH_3CO.CN$, and by this reaction, its constitution, which was formerly doubtful, has been ascertained.[3]

For its preparation a considerable quantity of tartaric acid is heated in a large iron pan and the mass constantly stirred until it begins to swell up and turn brown. It is then allowed quickly to cool and the solid mass broken up into small pieces which are subjected to dry distillation in a retort.[4] The pyroracemic acid is separated from the pyrotartaric and acetic acids also contained in the distillate, by fractional distillation. This process must, however, not be repeated too often, as the acid undergoes partial decomposition.

Pyruvic acid is a liquid having a pungent smell resembling that of both acetic acid and of extract of meat. It boils at about 165° and at 18° has a specific gravity of 1·288. On standing, it gradually passes into a syrup-like mass, and this change takes place quickly on heating. The acid is also separated in this form from its salts by means of acid. This form is not volatile and is probably a polymeric modification. Pyroracemic acid combines with nascent hydrogen to form lactic acid,[5] and with bromine in the cold to form dibromlactic acid.[6] On warming, however, it forms substitution-products.[7] Baryta-water produces in its aqueous solutions a precipitate, and when carbon dioxide is passed through this liquid, the barium salt of the dibasic and *hydruvic acid*, $C_6H_{10}O_7$, is formed in solution. This is formed by the union of two molecules of pyroracemic acid with water. On boiling with baryta-water on the other hand, other acids are formed which will be described later on.

[1] *Pogg. Ann.* xxxvi. 1.
[2] Moldenhauer, *Ann. Chem. Pharm.* cxxxi. 338.
[3] Claisen and Shadwell, *Ber. Deutsch. Chem. Ges.* xi. 1563.
[4] Böttinger, *Ann. Chem. Pharm.* clxxii. 240.
[5] Wislicenus, *ib.* cxxvi. 227; Debus, *ib.* cxxvii. 332.
[6] Wichelhaus, *Ber. Deutsch. Chem. Ges.* i. 264; Wislicenus, *Ann. Chem. Pharm.* cxlviii. 218; Clermont, *Bull. Soc. Chim.* xix. 103; Bodewig, *Jahresb.* 1879, 609; Grimaux, *Bull. Soc. Chim.* xxi. 393; Klimenko, *Journ. Russ. Chem. Ges.* viii. 125.
[7] Böttinger and Fittig, *Ber. Deutsch. Chem. Ges.* v. 956.

The salts which are termed *pyruvates* or *pyroracemates*, crystallize only when they are prepared in the cold. When their solutions are heated they pass into gum-like masses. These have been chiefly investigated by Berzelius, and the following are the most characteristic. *Sodium Pyruvate*, $C_3H_3O_3Na$, crystallizes in elastic prisms or tables, and is almost insoluble in alcohol. *Calcium Pyruvate*, separates out in crystals on evaporating its solution in the cold. If warmed even by the hand a gum-like mass is produced.

*Copper Pyruvate*, $(C_3H_3O_3)_2Cu + H_2O$. Copper carbonate dissolves in the aqueous acid forming a green liquid, and when the solution becomes saturated, the salt separates out as a sea-green powder. If a crystal of copper sulphate be brought into a solution of the sodium salt, it becomes covered with a *white* powder, which when dried over sulphuric acid becomes light-blue and has the same composition as the green salt.

*Silver Pyruvate*, $C_3H_3O_3Ag$, is difficultly soluble in cold water, but can be crystallized however from boiling solution. If the solution be allowed to cool in the dark, large glistening milk-white scales are deposited which soon become brown on exposure to light. If ammonium pyruvate solution be precipitated with silver nitrate, the silver salt separates out as a thick jelly; 300 grams of the salt dissolved in ten liters of water yield in this way such a stiff paste that a glass rod stands upright in it.[1]

*Iron Pyruvate.* If a crystal of green vitriol be brought into a solution of the sodium salt the liquid becomes at once dark red, and if the air be excluded, the *ferrous* salt separates out after some time in dark red crystals which dissolve with difficulty in water, yielding a yellow solution. If iron be dissolved in the warm dilute acid the solution soon becomes of a dark red colour and at last opaque. This liquid dries on evaporation to an almost black mass which is soluble in water.

The *ferric* salt obtained by dissolving ferric hydroxide in the acid is also a red soluble mass. Alkalis do not precipitate its solution.

*Methyl Pyruvate*, $C_3H_3O_3(CH_3)$, is formed by the action of methyl iodide on the silver salt. It is a liquid, smelling like acetone, boiling at 134°—137°, and having at 0° a specific gravity of 1·154 (Oppenheim). The ethyl ether is formed by the action of sulphuric acid on an alcoholic solution of the acid. It is

[1] Oppenheim, *Ber. Deutsch. Chem. Ges.* v. 1051.

a liquid possessing a peculiar smell, partially decomposes on distillation, and is wholly decomposed by water.[1]

As a ketonic acid pyroracemic acid combines with the acid sulphites of the alkali-metals forming crystallizable compounds.[2] Of these the sodium compounds may be mentioned.

$C_3H_4O_3+NaHSO_3$ is formed when pyroracemic acid and acid sodium sulphite are brought together. The solution decomposes on boiling with evolution of sulphur dioxide.

$C_3H_3ONa+NaHSO_3+H_2O$ is formed when the normal sulphite is used. On heating it intumesces to a sponge-like mass.

*a-Dichlorpropionic Acid*, $CH_3.CCl_2.CO_2H$. The chloride of this acid is formed by the action of phosphorus pentachloride,[3] or trichloride,[4] on pyroracemic acid. It is a pungent smelling liquid which boils between 105°—115°, and is quickly decomposed by water with formation of dichlorpropionic acid. This latter substance is best obtained from its nitril, which is formed by chlorinating propionitril. This boils from 103°—107°, and is a liquid which when boiled with sulphuric acid diluted with an equal volume of water is converted into the acid. This is a liquid which is soluble in water and which boils at 185°—190°, and forms crystals at 0°. Heated with water to 120°—150° it is converted into pyroracemic acid.[5]

*a-Dibrompropionic Acid*, $CH_3CBr_2CO_2H$, is formed by heating propionic acid with bromine to 190°—220°. It crystallizes in quadratic tables melting at 71°, and boils with slight decomposition at 221°. Its salts are tolerably stable.[6]

## MALONYL COMPOUNDS.

564 *Malonic Acid*, $CH_2(CO_2H)_2$, was first obtained by Dessaignes by oxidizing malic acid, $CO_2H.CH(OH).CH_2.CO_2H$, with potassium dichromate.[7] Baeyer then obtained it from uric acid,[8] and it was synthetically prepared simultaneously by Kolbe and

[1] Böttinger, *Ber. Deutsch. Chem. Ges.* xiv. 316.
[2] *Journ. Prakt. Chem.* [2], xvii. 241.
[3] Klimenko, *Ber. Deutsch. Chem. Ges.* iii. 465.
[4] Beckurts and Otto, *ib.* xi. 386.
[5] Beckurts and Otto, *ib.* ix. 1876; x. 263, 1503, 1952; xi. 386.
[6] Friedel and Machuca, *Ann. Chem. Pharm.* Suppl. ii. 72; Phillipi and Tolens, *ib.* clxxi. 315.
[7] *Comptes Rendus*, xlvii. 76; *Ann. Chem. Pharm.* cvii. 251.
[8] *Ib.* cxxx. 143.

H. Müller.[1] They obtained it by heating its nitril, cyanacetic acid (a body which will be described further on), with potash. This method of preparation was elaborated by various chemists.[2] According to Conrad the best mode of preparation is the following:—100 grams of monochloracetic acid dissolved in 200 cc. of water are neutralized with pure carbonate of potash or soda, and to this 80 grams of finely powdered and pure potassium cyanide are added, and the whole warmed. A violent reaction soon occurs, some hydrocyanic acid being evolved. In order, however, to complete the decomposition of the salt, heat must be employed for two hours on a water-bath, the water evaporating being replaced, and then 100 grams of caustic potash added, when an immediate evolution of ammonia takes place. It is then further heated, until the smell of this gas ceases, the whole neutralized with hydrochloric acid and calcium chloride added, which yields a voluminous precipitate, which soon becomes crystalline. This is then washed with boiling water and decomposed with the calculated quantity of oxalic acid. The filtrate is then evaporated, and the residue extracted with ether.[3]

Malonic acid is also formed by oxidizing propylene, $C_3H_6$, allylene, $C_3H_4$, and amylene, $C_5H_{10}$, with potassium permanganate.[4]

It is easily soluble in water and alcohol, and crystallizes in triclinic tables or laminæ. It melts at 132°, and decomposes at a higher temperature into carbon dioxide and acetic acid. Its salts have been carefully examined by Finkelstein.

*Potassium Malonate*, $C_3H_2O_4K_2$, is deliquescent. The acid salt, $2C_3H_2O_4HK+H_2O$, crystallizes in large prisms which do not undergo alterations in the air. *Acid Sodium Malonate*, $2C_3H_2O_4NaH+H_2O$, is deposited in large transparent crystals. *Calcium Malonate*, $2C_3H_2O_4Ca+7H_2O$, is very difficultly soluble in water, and crystallizes in small transparent needles. *Barium Malonate*, $C_3H_2O_4Ba+H_2O$, forms a silky radiating crystalline mass, and is also difficultly soluble in water, but dissolves readily in acetic acid. The other malonates are most of them slightly soluble in water.

[1] *Ann. Chem. Pharm.* cxxxi. 348 and 350; *Journ. Chem. Soc.* [2], ii. 79.

[2] Finkelstein, *Ann. Chem. Pharm.* cxxxiii. 338; Heintzel, *ib.* cxxxix. 129; H. von. Müller, *Journ. Prakt. Chem.* xix. 326; Grimaux and Tscherniak, *Bull. Soc. Chim.* xxxi. 338.

[3] *Ann. Chem. Pharm.* cciv. 125.

[4] *Compt. Rend.* lxiv. 36.

*Ethyl Malonate*, $C_3H_2O_4(C_2H_5)_2$, is best obtained by pouring eight parts of absolute alcohol on to three parts of the well-dried calcium salt, the whole being saturated with hydrochloric acid, and after standing for some time heated on the water-bath and hydrochloric acid gas again led into it. The alcohol is then allowed to evaporate, the residue neutralized with carbonate of soda and the ether separated by addition of water, dried, and purified by fractional distillation (Conrad).

It is a faintly aromatic-smelling liquid having a bitter taste, boiling at 195° and having at 18° a specific gravity of 1·068.

*Sodium Ethyl Malonate*, $CHNa(CO_2.C_2H_5)_2$, is obtained by the action of an alcoholic solution of sodium ethylate on the foregoing compound:

$$CH_2(CO_2.C_2H_5)_2 + NaO.C_2H_5 = CHNa(CO_2.C_2H_5)_2 + HO.C_2H_5.$$

It crystallizes in white glistening needles.[1]

It has already been stated that the sodium compound is used for the synthesis of the homologues of malonic acid, and for that of the higher fatty acids (Part I. page 180).

If ethyl carbonate be allowed to act upon this body *ethyl methenyl tricarbonate*, $CH(CO_2.C_2H_5)_3$ is formed. This is a pleasantly smelling liquid boiling at about 260°. It is decomposed by caustic potash into potassium malonate, potassium carbonate, and alcohol.[2]

*Ethyl Chlormalonate*, $CHCl(CO_2.C_2H_5)_2$, is formed by the action of chlorine upon ethyl malonate. It is a liquid boiling at 221°—222°.[3]

565 *Cyanacetic Acid*, $CO_2H.CH_2.CN$, is the nitril of malonic acid and, as has been stated, was obtained simultaneously by Kolbe and Hugo Müller, and then examined by many other chemists.[4] In order to prepare it, the operation is conducted in the first place as in the preparation of malonic acid, by acting upon the potassium salt of chloracetic acid with potassium cyanide. The solution is then evaporated, the residue acidified with sulphuric acid and shaken with ether. It forms yellow crystals, easily soluble in water and alcohol, melting at 55° and decomposing into carbon dioxide and acetonitril when more strongly heated. If the potassium salt of the acid be electrolyzed it decomposes into

[1] Conrad, *Ann. Chem. Pharm.* cciv. 129.
[2] Conrad, *Ber. Deutsch. Chem. Ges.* xii. 1236.
[3] Conrad and Bischoff, *ib.* xiii. 600.
[4] Meeves, *Ann. Chem. Pharm.* cxliii. 201; van't Hoff, *Ber. Deutsch. Chem. Ges.* vii. 1382.

hydrogen, carbon dioxide, and ethylene dicyanide (succinonitril), $C_2H_4(CN)_2$.[1]

*Ethyl Cyanacetate,* $CO_2(C_2H_5)CH_2.CN$, is obtained by warming potassium cyanide with an alcoholic solution of ethyl chloracetate or by passing hydrochloric acid into an alcoholic solution of cyanacetic acid. It is a heavy, almost odourless liquid boiling at 207°.

*Cyanacetyl Bromide,* $CN.CH_2.COBr$. This compound is obtained by acting with silver cyanide on a solution of bromacetyl bromide in chloroform, the isomeride, *bromacetyl cyanide,* $CH_2Br.CO.CN$, being at the same time produced. This can be separated from the former, compound, by shaking with ether in which it dissolves.

Bromacetyl cyanide crystallizes in monoclinic tables, melting at 77°—79° and is decomposed by water into hydrocyanic acid and bromacetic acid. Cyanacetyl bromide, on the other hand, crystallizes in long needles, and is decomposed by water and more quickly by alkalis with formation of malonic acid:[2]

$$CN.CH_2.COBr + 3H_2O = CO_2H.CH_2.CO_2H + NH_4Br.$$

*Dibrom-malonic Acid,* $CBr_2(CO_2H)_2$. If bromine is added to an aqueous solution of malonic acid, decomposition takes place, and when it is used in excess, tribromacetic acid and carbon dioxide are formed. If, however, a solution in chloroform be employed, dibrommalonic acid is formed, crystallizing in deliquescent needles, and melting at 126°—128°.

*Nitrosomalonic Acid,* $C_3H_3(NO)O_4$, was first obtained by Baeyer by decomposition of the corresponding urea, violuric acid (for which see *uric acid*), with potash. It forms glistening needles easily soluble in water, which melt on heating, and then explode with a loud noise. When boiled with water, it decomposes as follows:

$$CH(NO)(CO_2H)_2 = CHN + H_2O + 2CO_2.$$

*Amidomalonic Acid,* $C_3H_3(NH_2)O_4$; is formed when the foregoing compound is brought into contact with sodium amalgam and water. It is easily soluble in water and crystallizes in large glistening prisms. When it is heated, or its aqueous solution boiled, it decomposes completely into carbon dioxide and amido-acetic acid.

[1] Moore, *Ber. Deutsch. Chem. Ges.* iv. 519.
[2] Hübner, *Ann. Chem. Pharm.* cxxix. 124.

*Oxymalonic Acid*, $C_3H_3(OH)O_4$, was prepared by Dessaignes by the spontaneous decomposition of the so called nitro-tartaric acid, and known as tartronic acid.[1] It is also formed by the reduction of mesoxalic acid[2] and by acting with potash on ethyl chlormalonate:[3]

$$CHCl(CO_2.C_2H_5)_2 + 3KOH = CH(OH)(CO_2K)_2 + KCl + 2C_2H_5OH.$$

It can be obtained synthetically by bringing together glyoxalic acid and potassium cyanide and boiling the product with baryta water.[4] It is easily soluble in water, crystallizes in large transparent prisms, and is decomposed at 182° into carbon dioxide and glycolide:

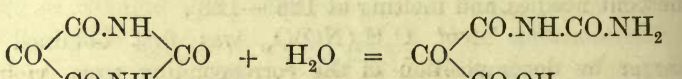
$$2C_3H_4O_5 = C_4H_4O_4 + 2CO_2 + 2H_2O.$$

566 *Mesoxalic Acid*, $CO(CO_2H)_2$, was first obtained by Liebig and Wöhler as a product of decomposition of mesoxalyl urea (alloxan), a body obtained by oxidizing uric acid with nitric acid.[5] It is also formed by the action of iodine on amidomalonic acid.[6]

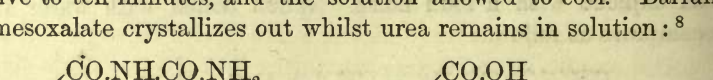
$$CH(NH_2)(CO_2H)_2 + I_2 + H_2O = CO(CO_2H)_2 + NH_4I + HI.$$

It is also formed by the action of silver oxide on dibrompyroracemic acid.[7]

In order to prepare it, a warm aqueous solution of alloxan is treated with baryta water, not in excess, when barium alloxanate separates out:



The salt thus obtained is boiled with 200 parts of water for five to ten minutes, and the solution allowed to cool. Barium mesoxalate crystallizes out whilst urea remains in solution:[8]



The acid is then liberated from the barium salt by sulphuric acid. It forms deliquescent crystals, having the formula

[1] *Ann. Chem. Pharm.* lxxxii. 362; lxxxix. 399.
[2] Deichsel, *Journ. Prakt. Chem.* xciii. 205.
[3] Conrad and Bischoff, *Ber. Deutsch. Chem. Ges.* xiii. 600.
[4] Böttinger, *ib.* xiv. 729.
[5] *Ann. Chem. Pharm.* xxvi 298.
[6] Baeyer, *ib.* cxxxi. 298.
[7] Deichsel, *Journ. Prakt. Chem.* xciii. 193.
[8] Wislicenus, *ib.*

$C_3H_2O_5+H_2O$, which melt at 115° without losing water. From this, as well as from the fact that its salts retain water with great force, it appears very probable that the acid has a composition analogous to that of glyoxalic acid (p. 103), according to which its formula would be $C(OH)_2(CO_2H)_2$. If the aqueous solution be heated above 70°, decomposition takes place with evolution of carbon dioxide; and when boiled with silver oxide, the following reaction takes place:

$$CO_2H.CO.CO_2H + Ag_2O = CO_2H.CO_2H + CO_2 + Ag$$

*Ammonium Mesoxalate*, $C_3O_5(NH_4)_2$, separates out in grains when ammonia is added to an aqueous solution of the acid. It is anhydrous and perhaps is the ammonium salt of the yet unknown mesoxamic acid, $CO(NH_2)C(OH)_2CO_2H$.

*Barium Mesoxalate*, $2C_3O_5Ba+3H_2O$, forms microscopic prisms which are scarcely soluble in cold, and only slightly soluble in hot water. It does not lose water till 170° when it partially decomposes.

*Lead Mesoxalate*, $C_3O_5(PbOH)_2$, is a white, light insoluble powder. The normal salt does not appear to exist.

*Silver Mesoxalate*, $C_3O_5Ag_2+H_2O$, is a white amorphous precipitate, which soon changes to tufts of yellowish needles, and is decomposed on exposure to light.

*Ethyl Mesoxalate*, $C_3H_5(C_2H_5)_2+H_2O$, is formed by heating the silver salt with an alcoholic solution of ethyl iodide. It is a heavy yellow oil which decomposes on heating. It is very soluble in water and is soon decomposed into alcohol and mesoxalic acid. The presence of water in this ether is a strong argument for the formula which has already been given for the acid. According to this the ether has the constitution $C(OH)_2.(CO.OC_2H_5)_2$.

# THE BUTYLENE COMPOUNDS.

567 In 1815 Taylor noticed that when fats or oils are strongly heated, a gas of high illuminating power is obtained. This observation led to the development of a new branch of industry, for this oil-gas was pumped into strong copper vessels under a pressure of about 30 atmospheres, and these were carried to the houses of the consumers, where the gas, known as portable gas, was burnt as an illuminating agent.

During the process of manufacturing this portable gas a liquid was obtained, which was investigated in 1825 by Faraday, who discovered in it two hydrocarbons. To one of these, now known as benzene, he gave the name of *Bicarburet of Hydrogen*, and the other he termed "a new hydrocarbon," without giving it any special name. He observed that the second one was gaseous at the ordinary temperature, and on burning it he found that one volume of this gas requires six volumes of oxygen, yielding four volumes of carbon dioxide. Accordingly Faraday concluded that the "new hydrocarbon" has the same composition as olefiant gas, but he noticed that it has a specific gravity between 27 and 28 (H=1), or double that of olefiant gas. Like this latter compound the new hydrocarbon combines with an equal volume of chlorine to form an oily liquid, but the oil thus obtained contains twice the quantity of carbon and hydrogen to the same quantity of chlorine as Dutch liquid.[1] To this hydrocarbon, $C_4H_8$, Berzelius gave the name of *ditetryl*. Kolbe [2] by the electrolysis of potassium valerate afterwards obtained a compound of similar constitution together with valyl (di-isobutyl, Part I. p. 654), and Wurtz [3] found a similar compound amongst the products of decomposition of amyl alcohol at a red-heat. Soon after this, Berthelot [4] observed that this hydrocarbon, which was also termed *tetrylene*, *butyrene*, and

[1] *Phil. Trans.* 1825, p. 440.
[2] *Ann. Chem. Pharm.* lxix. 269.
[3] *Ib.* civ. 240.
[4] *Ib.* cviii. 200.

*butylene*, is formed when sodium acetate or calcium oleate is heated with soda lime, and that it also occurs as a product of decomposition of other organic bodies at high temperatures. According to Hahn[1] butylene is also found, together with its homologues, amongst the products which are obtained by dissolving cast-iron in acids, a fact which has been subsequently confirmed by Cloëz.[2]

At first it was believed that the butylenes obtained by these various processes were identical, but other investigations have shown that three isomeric modifications exist, viz.—

(1) *α*-Butylene, or Ethylethylei

$$CH_3.CH_2.CH = CH_2.$$

(2) *β*-Butylene, or Symmetrical Dimethylethylene.

$$CH_3CH = CH.CH_3.$$

(3) Isobutylene, or Unsymmetrical Dimethylethylen

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = CH_2.$$

568 *α-Butylene*, or *Ethyl Ethylene*, $CH_3.CH_2CH = CH_2$. This body was first obtained by Wurtz by heating bromethylene (vinyl bromide), $C_2H_3Br$, with zinc ethide, and described as *vinyl-ethyl*.[3] It is also obtained together with ethyl-butyl ether when primary butyl iodide is heated with alcoholic potash.[4] It is a gas at the ordinary temperature, but it can be condensed by cold to a liquid boiling at 5°.

*α-Butylene Bromide*, $CH_3.CH_2.CHBr.CH_2Br$, is a colourless liquid boiling at 166° and having a specific gravity of 1·8053.

*α-Butylene Glycol*, $CH_3.CH_2.CH(OH).CH_2(OH)$, is obtained by treating the bromide with silver acetate and glacial acetic acid and decomposing the product with caustic baryta. It is a thick liquid soluble in water, boiling at 191°—192°, and having at 0° a specific gravity of 1·0189 (Saytzew and Grabowsky).

Ethyl chlorether, $CH_3.CH_2.CH(OC_2H_5)CH_2Cl$, and biethyl ether, $CH_3.CH_2.CH(OC_2H_5)CH_2(OC_2H_5)$, already described, are also *α*-butylene compounds.

*β-Butylene*, or *Symmetrical Dimethyl Ethylene*, $CH_3.CH = CH.CH_3$, is obtained by heating secondary butyl iodide with

[1] *Ann. Chem. Pharm.* cxxix. 57. [2] *Compt. Rend.* lxxviii. 1565.
[3] *Ann. Chem. Pharm.* clii. 21.
[4] Lieben and Rossi, *ib.* clviii. 164; Grabowsky and Saytzew, *ib.* clxxix. 330.

alcoholic potash.[1] It is also formed when a mixture of methyl iodide and allyl iodide, $CH_2 - CH - CH_2I$, is heated with sodium.[2] In this case the formation of *a*-butylene might be expected, and a small quantity of this substance is formed, as well as some isobutylene,[3] but the chief product is the *β*-compound, and hence a molecular interchange has taken place. Its formation from isobutyl alcohol is still more remarkable. For this purpose this liquid is allowed to drop on to heated zin chloride, and the gases evolved are passed through sulphuric acid diluted with one-half its volume of water, the isobutylene which is formed at the same time being absorbed. The unabsorbed gases are passed into bromine, and from the product *β*-butylene bromide is obtained by fractional distillation. If this body be treated with sodium the pure hydrocarbon is obtained, boiling at $+1°$ and having a specific gravity at $-13°{\cdot}5$ of 0·635. It solidifies in a vacuum over a mixture of ether and solid carbonic acid to a crystalline mass.

*β-Butylene Bromide*, $CH_3.CHBr.CHBr.CH_3$, is a liquid boiling at 158° and having a specific gravity at 0° of 1·821. When heated with 20 times its volume of water together with lead oxide to 140°—150° it is converted into methyl-ethyl ketone (Eltekow).

*β*-Butylene glycol has not yet been prepared. Another glycol standing between it and the *a*-compound has however been obtained, to which there is no corresponding olefine.

*γ-Butylene Glycol*, $CH_3.CH(OH)CH_2.CH_2(OH)$, is formed in small quantity, together with ethyl alcohol, when an aqueous solution of acetaldehyde is treated with sodium amalgam and the liquid kept slightly acid by addition of hydrochloric acid.[4] In this case *β*-oxybutyraldehyde, a body afterwards to be described, is first formed, and this combines with nascent hydrogen to form the glycol.[5] It is a thick liquid having a sweet taste, and is not soluble in water but dissolves in ether. It boils at 203°·5—204.°

569 *Isobutylene*, or *Unsymmetrical Dimethyl Ethylene*, $(CH_3)_2C{=}CH_2$, was first obtained by Kolbe by electrolysis of calcium valerate. It is also found, probably together with isomerides, in the products of decomposition of amyl alcohol by heat.[6] It is

[1] De Luynes, *Ann. Chem. Pharm.* cxxix. 200; cxxxii. 275; Lieben, *ib.* cl. 108.
[2] Wurtz, *ib.* cxliv. 235.
[3] Grosheintz, *Bull. Soc. Chim.* xxix. 201; Le Bel and Greene, *ib.* xxix. 306.
[4] Kekulé, *Ann. Chem. Pharm.* clxii. 310. [5] Wurtz, *Bull. Soc. Chim.* xx. 4.
[6] Butlerow, *Ann. Chem. Pharm.* cxlv. 277.

likewise formed easily when isobutyl iodide or tertiary butyl iodide is heated with alcoholic potash. The simplest method of obtaining it is however to heat together a mixture of 10 parts of isobutyl alcohol, 10 parts of sulphuric acid, 4 parts of potassium sulphate, and 16 parts of calcium sulphate.[1] According to J. Lermontow a better yield is obtained by adding 2 parts of water, and using powdered glass instead of calcium sulphate.[2] Konowalow found that this product contains about one-third of $\beta$-butylene and a small quantity of a paraffin which is probably isobutane.[3] Isobutylene is a gas which has an unpleasant smell like coal gas, and is condensed by pressure or cold to a liquid which boils at $-6°$.[4]

*Isobutylene Chloride*, $C_4H_8Cl_2$, is an oily liquid having a smell resembling that of ethylene chloride and boiling at 123° (Kolbe).

*Isobutylene Chlorhydrin*, $(CH_3)_2CCl.CH_2.OH$, is obtained by the union of hypochlorous acid with isobutylene. It is an aromatic-smelling liquid boiling at 137°, and being converted by the action of sodium amalgam and water into isobutyl alcohol.[5]

*Isobutylene Bromide*, $C_4H_8Br_2$, boils at 148°—149° and has a specific gravity at 14° of 1·798. When heated with lead oxide and 15 to 20 times its volume of water to 140°—150° isobutyl aldehyde is formed, together with a small quantity of isobutylene glycol.[6] Alcoholic potash converts the bromide into *bromisobutylene*, $(CH_3)_2C{=}CHBr$, a body boiling at 91°, and yielding isobutyric acid on heating with silver oxide and water (Butlerow).

*Isobutylene Glycol*, $(CH_3)_2C(OH)CH_2(OH)$, is a liquid resembling common glycol, obtained by heating the bromide with water and potassium carbonate. It boils at 176°—178° and has at 0° a specific gravity of 1·0219.[7]

Wurtz obtained a butyl glycol from butylene obtained by the decomposition of amyl alcohol at a red-heat. It boils at 183°—184°,[8] and is probably a mixture.

*Nitro-isobutylene*, $(CH_3)_2C{=}CH(NO_2)$, is formed by the action

[1] Puchot, *Compt. Rend.* lxxxv. 757.
[2] *Ann. Chem. Pharm.* cxcvi. 117.
[3] *Bull. Soc. Chim.* [2], xxxiv. 333.
[4] Butlerow, *Zeitsch. Chem.* 1870, 236.
[5] Butlerow, *Ann. Chem. Pharm.* cxliv. 26
[6] Elketow, *Journ. Russ. Chem. Ges.* x. 214
[7] Nevolé, *Bull. Soc. Chim.* xxvii. 63.
[8] *Ann. Chim. Phys.* [3], lv. 400.

of concentrated nitric acid on trimethyl carbinol. It is a yellowish oil which boils with partial decomposition at 154°—158°, and has a very pungent smell and burning taste. It is almost insoluble in water but dissolves readily in alkalis. With alcoholic soda it yields the compound $C_4H_6NaNO_2$, a yellow powder which on heating deflagrates, and decomposes on standing, changing its colour to brown. If nitro-isobutylene be heated with water to 100° it decomposes into acetone and nitromethane, and when heated with hydrochloric acid, it yields ammonia, hydroxylamine, carbon dioxide and other products which have not yet been investigated.[1]

## TRICHLORBUTIDENE COMPOUNDS.

570 *Trichlorbutidene Oxide, Trichlorbutyraldehyde,* or *Butyl Chloral,* $CH_3.CHCl.CCl_2.COH$, was first obtained by Krämer and Pinner[2] by acting with chlorine on acetaldehyde, and described as *croton chloral,* $C_4H_3Cl_3O$. Its correct composition was then recognised by Pinner,[3] who also explained its formation. Two molecules of aldehyde first unite together with separation of water and formation of croton aldehyde:

$$\begin{matrix} CH_3 \\ | \\ COH \\ \\ CH_3 \\ | \\ COH \end{matrix} \quad = \quad \begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ COH \end{matrix} \quad + \quad H_2O.$$

Chlorcroton-aldehyde, $CH_3.CH{=}CCl.COH$, is then formed, and this unites with one molecule of chlorine. The compound is best obtained by passing chlorine into paraldehyde, which is well cooled and afterwards heated to 100° as long as action is observed. More alcohol is added to the product, and this neutralized with calcium carbonate, when the whole is distilled and the corresponding hydrate obtained, and this on heating in a stream of hydrochloric acid yields pure butyl chloral. It is an oily pungent-smelling liquid, boiling at 164°—165°, and having a specific gravity of 1.3956 at 20°.

[1] Haitinger, *Ann. Chem. Pharm.* cxciii. 366.
[2] *Ber. Deutsch. Chem. Ges.* iii. 386 and 790.
[3] *Ann. Chem. Pharm.* clxxix. 21.

*Trichlorbutidene Glycol*, or *Butyl Chloral Hydrate*, $CH_3.CHCl.CCl_2.CH(OH)_2$, is easily obtained by the union of the foregoing compound with water. It crystallizes in tablets which are difficultly soluble in hot water. It fuses at 78°, and is easily volatile, yielding a vapour which excites a flow of tears. Given internally it acts similarly to chloral hydrate, and is said to have been used with good effect in certain cases. In other respects butyl chloral presents the greatest analogy to common chloral. Potash solution decomposes it in the cold with formation of allylene dichloride, $CH_3CCl :: CHCl$, and potassium formate. Heated with fuming nitric acid, *trichlorbutyric acid*, $CH_3.CHCl.CCl_2.CO_2H$, is formed, a body tolerably soluble in water, and crystallizing in needles which melt at 60°, the acid boiling between 236° and 238°, and forming salts which are easily decomposed.[1]

## THE OXYBUTYRIC ACIDS.

571 *a-Oxybutyric Acid*, $CH_3.CH_2.CH(OH).CO_2H$, was first obtained from brombutyric acid (Part I. p. 579) by acting on it with water and silver oxide.[2] In order to prepare it, brombutyric acid is boiled with baryta solution, the barium precipitated by sulphuric acid and the oxybutyric acid extracted from the solution by shaking with ether. The crude acid is then converted into the zinc salt, $(C_4H_7O_3)_2Zn+2H_2O$, crystallizing in small prisms and difficultly soluble in cold water, and this is then decomposed by sulphuretted hydrogen.[3]

*a*-Oxybutyric acid is also formed when propionaldehyde is mixed with an excess of aqueous hydrocyanic acid and allowed to stand for some days at 0°. One and a half times its volume of hydrochloric acid of specific gravity 1·185 is added, and the whole allowed to stand at the ordinary temperature for some days, and then heated for some hours to 60°—70° and the acid removed by shaking with ether.[4]

It is a crystalline deliquescent mass melting at 42°–42°·5,

[1] Krämer and Pinner, *Ber. Deutsch. Chem. Ges.* iii. 389; Judson, *ib.* iii. 785; Kahlbaum, *ib.* xii. 2337; Gazzorolli-Thurnlak, *Ann. Chem. Pharm.* clxxxii. 181.

[2] Naumann, *ib.* cxix. 115; Friedel and Machuca, *ib.* cxx. 279.

[3] Markownikow, *ib.* clix. 242.

[4] Prizibytek, *Journ. Russ. Chem. Ges.* viii. 335; *Ber. Deutsch. Chem. Ges.* ix. 1348.

beginning to sublime at 60°–70°, and boiling at 255°–260° with partial decomposition. On oxidation it yields propionaldehyde and propionic acid.[1]

572 *β-Oxybutyric Acid,* $CH_3.CH(OH).CH_2.CO_2H$, was first obtained by Wislicenus by acting with sodium amalgam and water on ethyl acetacetate [2] (p. 172). It is also formed when propylene chlorhydrin is heated to 100° with potassium cyanide and spirit of wine, and the nitril which is thus formed decomposed with caustic potash.[3] In order to separate it from alkali salts which are formed at the same time, it is acidified with sulphuric acid and shaken up with ether; the ethereal solution depositing the acid as a viscid deliquescent syrup, which volatilizes in a current of steam, and when heated by itself is converted into *α*-crotonic acid. The zinc salt is, like most of the *β*-oxybutyrates, amorphous.

*β-Oxybutyraldehyde,* $CH_3.CH(OH).CH_2.COH$. This compound, which is the only known aldehyde in the lactic acid series, was obtained by Wurtz by gradually adding 2 parts of hydrochloric acid of specific gravity 1·16 cooled to –10°, to a mixture of equal parts of hydrochloric acid and aldehyde cooled to 0°. The mixture was allowed to stand for some days at the ordinary temperature, then neutralized with carbonate of soda, shaken up with ether, and the residue remaining on evaporation was distilled in a vacuum. The formation of this body, which was termed *aldol* (aldehyde alcohol) by Wurtz, is explained by the following equations:

(1) $CH_3COH + HCl = CH_3CH(OH)Cl.$

(2) $CH_3.CH.(OH)Cl + CH_3.COH = CH_3.CH(OH)CH_2COH + HCl.$

It is a thick liquid which at 0° is so tenacious that the vessel containing it may be overturned without its running out. It is easily soluble in water, and has a bitter aromatic taste. Under ordinary pressure it cannot be distilled without change, as it decomposes above 135°, into water and croton aldehyde. It quickly reduces ammoniacal silver solution with formation of a silver mirror, and production of *β*-oxybutyric acid, and unites with nascent hydrogen, forming *β*-butylene glycol.

[1] Ley, *Ber. Deutsch. Chem. Ges.* x. 230.
[2] *Ann. Chem. Pharm.* cxlix. 205.
[3] Markownikow, *ib.* cliii. 237.

On standing it undergoes spontaneous change into *paraldol*, a body crystallizing in triclinic prisms, and this on heating under diminished pressure is again transformed into aldol.

*Aldol-Ammonia*, or *Oxydibutidene Hydroxyamine*,

$$CH_3.CH(OH).CH_2CH\begin{cases}OH\\NH_2,\end{cases}$$

is obtained by passing ammonia into an ethereal solution of aldol. It is a syrupy liquid, which dries up in a vacuum to a resinous mass.

*Dialdan*, $C_8H_{14}O_3$, is formed when the mixture of aldehyde and hydrochloric acid, used for the preparation of aldol, is allowed to stand for some time.

It forms crystals which are slightly soluble in cold water, but dissolve in boiling alcohol and melt at 130°. Like aldehyde it reduces ammoniacal silver solution, and it is oxidized by potassium permanganate with formation of monobasic *dialdanic acid*, $C_8H_{14}O_4$, a body easily soluble in water, and crystallizing in monoclinic prisms, which melt at 80°.[1]

When dialdan is treated with sodium amalgam in slightly acid solution, dialdan alcohol, $C_8H_{16}O_3$, is formed. This is a crystalline deliquescent mass melting at about 50° and boiling at 162°—165° under a pressure of 10mm. On heating with acetic anhydride, the diacetate, $C_8H_{14}(C_2H_3O)_2O_3$, is formed. The alcohol does not combine with bromine, and the dialdan compounds therefore do not not contain, as Wurtz formerly supposed, two doubly linked carbon atoms. He now gives the following formula to the alcohol :[2]

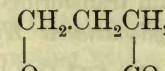
$$\begin{array}{c}CH_3.CH.CH_2.CH.CH_2.CH(OH)CH_2CH_2.OH.\\ \diagdown\quad\diagup\\ O\end{array}$$

When dialdan is heated with aqueous ammonia, the dyad base, $C_{16}H_{28}O_2N_2$, is formed. It is amorphous, easily soluble in water, and has an alkaline reaction and a very bitter taste.[3]

573 *γ-Oxybutyric Acid*, $CH_2(OH).CH_2.CH_2.CO_2H$. By the action of phosphorus pentachloride on succinic acid, $C_2H_4(CO_2H)_2$, the corresponding chloride, $C_2H_4(COCl)_2$, is obtained, and this when treated with glacial acetic acid and sodium amalgam yields

[1] *Bull. Soc. Chim.* [2], xvii. 436; xx. 4; *Compt. Rend.* lxxxiii. 255, 1259; lxxxvii. 45; *Bull. Soc. Chim.* xxviii. 170.
[2] *Compt. Rend.* xcii. 1371.
[3] *Ib.* xc. 1030.

the anhydride of the above oxybutyric acid, which probably possesses the following constitution :



It is a crystalline body boiling at 201°—203°, and when heated with baryta water it yields the crystalline deliquescent barium salt, from which the acid can be liberated by dilute sulphuric acid and withdrawn from solution by means of ether. On evaporating this solution the acid remains as a liquid, which on distillation yields water and the anhydride, which on oxidation yields succinic acid, and was formerly considered to be the aldehyde of this latter acid. The solution of the zinc salt yields a syrup on evaporation, which on standing solidifies to an imperfectly crystalline mass.

By the action of phosphorus iodide on the aqueous solution of the anhydride γ-iodobutyric acid is obtained, an oily liquid which is converted into normal butyric acid by the action of dilute sulphuric acid and sodium amalgam.[1]

574 *α-Oxyisobutyric Acid*, $(CH_3)_2.C(OH).CO_2H$, was first obtained by Wurtz by oxidizing amylene glycol, and termed by him butyl lactic acid.[2] Städeler afterwards obtained it by the action of hydrocyanic acid and hydrochloric acid on acetone, a mode of formation which is analogous to that of lactic acid from aldehyde, and termed it *acetonic acid*.[3] After this Frankland and Duppa obtained an acid of the same composition by heating methyl oxalate with methyl iodide and zinc, and to it they gave the name of *dimethyl oxalic acid*,[4] and Markownikow found that these acids are identical with that which he obtained by boiling bromisobutyric acid with baryta water.[5] Any one of these different methods may be employed for the preparation of the acid. A mixture of acetone, hydrocyanic acid and dilute hydrochloric acid is allowed to stand for three weeks. It is then boiled for three days in connection with a reversed condenser, the excess of acetone evaporated off on the water-bath, and the residue shaken with ether, the acid remaining after evaporation of the ether being converted into the zinc salt, and this in its turn decomposed by sulphuretted hydrogen.[6]

[1] Saytzew, *Journ. Prakt. Chem.* [2], xxv. 61.
[2] *Ann. Chem. Pharm.* cvii. 197.
[3] *Ib.* cxi. 320.
[4] *Ib.* cxxxiii. 80.
[5] *Ib.* cliii. 228.
[6] Markownikow, *ib.* clvi. 399.

To obtain it from methyl oxalate, amalgamated granulated zinc is covered with a mixture of the ether and methyl iodide, in the proportion of 1 to 2 molecules, and the mixture heated in absence of air for 96 hours to 30°—50°. To the crystalline mass water is gradually added and the whole boiled with an excess of caustic baryta. The dissolved iodine is removed by silver oxide, and the barium precipitated by carbon dioxide, the barium salt being obtained by concentrating the solution, and this again decomposed by sulphuric acid.[1]

If the acid is to be obtained from bromisobutyric acid, sodium carbonate should be employed in place of caustic baryta.[2]

Oxyisobutyric acid is very soluble in water, and crystallizes in large white prisms which melt at 79°, but begins to sublime at 50°. It boils without decomposition at 212°, and volatilizes easily in a current of steam. It has a strong acid taste and a peculiar cheese-like smell. Its crystalline salts are all easily soluble in water, with the exception of the zinc salt $(C_4H_7O_3)_2Zn + 2H_2O$, which crystallizes in six-sided microscopic laminæ, or in well-formed four-sided tables, dissolving at 15° in 160 parts of water, and being somewhat more soluble in boiling water.

*β*-Oxysobutyric Acid, $\begin{matrix} CH_2(OH) \\ CH_3 \end{matrix}\!\!>\!CH.CO_2H$, which ought, according to theory, to exist, is not known.

## THE KETONIC ACIDS.

575 *Propionyl Formic Acid*, $CH_3.CH_2.CO.CO_2H$. When propionyl chloride is heated with silver cyanide, its nitril or propionyl cyanide, $C_2H_5.CO.CN$, is formed. This is a liquid resembling acetyl cyanide; it boils at 108°—110°, and is decomposed by water into propionic acid and hydrocyanic acid. Propionyl formic acid is obtained by the action of hydrochloric acid upon this body. It is a peculiarly smelling oil which boils under a pressure of 25mm. at 74°—78°. Sodium amalgam and water convert it into *a*-oxybutyric acid. The majority of its salts are easily soluble in water and crystallize well, and this serves to distinguish this acid from its lower homologue, pyroracemic acid.[3]

[1] *Ann. Chem. Pharm.* cxxxv. 25. [2] Fittig, *ib.* cc. 68.
[3] Claisen and Moritz, *Ber. Deutsch. Chem. Ges.* xiii. 2121.

576 *Acetoacetic Acid*, $CH_3.CO.CH_2.CO_2H$, is not known in the free state. Ethers of it are however known, and of these the following are the most important.

*Ethyl Acetoacetate*, or *Acetoacetic Ethyl Ether*, $CH_3.CO.CH_2.CO_2.C_2H_5$. In the year 1863 Geuther commenced to study the action of sodium on ethyl acetate, and found that a crystalline compound having the formula $C_6H_9NaO_3$ is formed, together with sodium ethylate, hydrogen being at the same time evolved. If the first of these substances be heated with methyl or ethyl iodide, ether-like compounds are formed, whilst by the action of hydrochloric acid on this sodium compound a volatile liquid having the composition $C_6H_{10}O_3$ is produced, to which he at first gave the name of diacetic ether.[1] Later on, however, he found that one atom of hydrogen in this body can be replaced not only by sodium but by other metals, and he then considered the body to be ethyl diacetic acid, and the bodies obtained by the action of iodides on this he considered to be the ethers of this acid.[2]

In the meantime Frankland and Duppa,[3] without being acquainted with Geuther's investigations, occupied themselves with this subject, and likewise found that sodium acts upon acetic ether with evolution of hydrogen and formation of a crystalline mass. This mass they treated with ethyl iodide, and after the reaction was complete added water to it and distilled, and from this distillate obtained the following products:

(1) Diethyl ether, $(C_2H_5)_2O$.

(2) The ethyl ether of ethyl acetic acid, $(C_2H_5)CH_2.CO_2H$, which is identical with butyric acid.

(3) The ethyl ether of diethylacetic acid, $(C_2H_5)_2CH.CO_2H$, which is isomeric with caproic acid.

(4) Ethyl acetone-carbonic acid, $C_8H_{14}O_3$, a body identical with Geuther's ethyl diacetic ethyl ether, and it is converted by heating with baryta water into alcohol, carbon dioxide, and *ethyl acetone* $(C_2H_5)CH_2.CO.CH_3$.

(5) Diethyl-acetone acetic ether, $C_{10}H_{18}O_3$, a body which on heating with bases yields alcohol, carbon dioxide, and *diethyl-acetone*, $(C_2H_5)_2CH.CH.CO.CH_3$.

Similar compounds with other alcohol radicals were obtained by the employment of the iodides of methyl, isopropyl and amyl.

[1] *Jahresb. Chem.* 1863, 323. [2] *Ib.* 1865, 302.
[3] *Phil. Trans.* clvi. 37.

The formation of ethyl acetic acid and diethyl acetic acid and other simple and double substituted acetic acids was explained by the supposition that when sodium acts upon acetic ether the compounds $CH_2Na.CO_2C_2H_5$ and $CHNa_2.CO_2C_2H_5$ are formed, and that when the sodium in these is replaced by alcohol radicals the ethers of the higher fatty acid are produced.

The formation of ethyl carbonate of ethyl can also be readily explained. According to Geuther the formation of sodium ethyl diacetate, or sodacetone carbonate of ethyl as Frankland and Duppa called it is represented by the following equation:

$$2C_2H_5O.C_2H_3O + Na_2 = H_2 + C_2H_5.ONa + C_6H_9NaO_3.$$

But according to Frankland and Duppa it is probably formed as follows:

$$4\ \begin{matrix}CH_3\\|\\CO.OC_2H_5\end{matrix} + Na_2 = \begin{matrix}CH_3\\|\\CO\\|\\CHNa\\|\\CO.OC_2H_5\end{matrix} + 2C_2H_5.OH + H_2.$$

If the sodium be replaced by ethyl, ethyl carbonate of ethyl is formed, and this is decomposed by baryta water into ethyl acetone, alcohol, and carbon dioxide.

In this reaction disodacetonate of ethyl may be formed:

$$2\ \begin{matrix}CH_3\\|\\CO.OC_2H_5\end{matrix} + Na_2 = \begin{matrix}CH_3\\|\\CO\\|\\CNa_2\\|\\CO.OC_2H_5\end{matrix} + C_2H_5OH + H_2.$$

This can be converted by ethyl iodide into diethyl carbonate of ethyl which yields diethyl acetone when decomposed by alkalis.[1]

These views are generally accepted, and as in this case the action of sodium upon acetic ether is first to produce sodium acetoacetic ether, $CH_2Na.CO_2C_2H_5$, it was hoped by the action of acetyl chloride on the crude product to obtain larger quantities of Geuther's ethyl diacetic acid.[2] Hence it was termed acetyl acetic ether,[3] or shortly, acetacetic ether.

[1] *Phil. Trans.* xcvi. 37. [2] Lippmann, *Zeitsch. Chem.* 1869, 28.
[3] Wislicenus, *Ann. Chem. Pharm.* cxlix. 207.

Geuther had, however, in the meantime repeated his experiments and arrived at exactly the same conclusion as before. He in vain endeavoured to obtain the hypothetical sodium compound, the existence of which Frankland and Duppa assumed, and he was able to explain to a great extent some of the syntheses obtained by these chemists. He found in the first place that when pure sodium ethylate is heated with pure acetic ether a considerable quantity of "ethyl diacetic acid" is formed—

$$C_2H_5.ONa + 2C_4H_8O_2 = 2C_2H_5.OH + C_6H_9NaO_3.$$

Moreover, he observed that when the ethyl ether of this acid (ethyl acetone carbonate of ethyl) is heated with acetic ether and sodium ethylate, ethyl butyrate is formed:

$$C_6H_9(C_2H_5)O_3 + C_2H_5.ONa + C_2H_3O.OC_2H_5 = C_2H_3NaO_2 + 2C_4H_7O.OC_2H_5.$$

By the action of sodium on acetic ether the first compound which is produced is $C_6H_9NaO_3$, together with sodium ethylate. This latter acts further upon the acetic ether according to the first of the above equations. By the action of ethyl iodide ethyl acetone carbonate of ethyl is formed, and this is then converted according to the second equation into sodium acetate and ethyl butyrate. He also suggested that the latter compound yields the two other bodies, inasmuch as when treated with sodium ethylate, it behaves in a similar way to ethyl acetate.[1]

Further investigations on this subject have shown that when perfectly pure and absolutely dry acetic ether is made use of no hydrogen is evolved.[2] According to Oppenheim and Precht[3] this depends upon the fact that a part of the acetyl which separates from the acetic ether is reduced to sodium ethylate:

$$CH_3.CO- + Na + H_2 = CH_3.CH_2.ONa.$$

577 The researches of Wislicenus and his pupils however have thrown a clear light upon the changes which accompany the synthetical reactions discovered by Frankland and Duppa. The results to which they arrived have already been mentioned. (Part I., page 180.)

It is therefore sufficient here shortly to state that the ethyl sodacetacetate, $CH_3.CO.CHNa.CO.OC_2H_5$ is converted by acids

[1] *Jahresb.* 1868, 511.

[2] Wanklyn, *Journ. Chem. Soc.* [2], ii. 371; Ladenburg, *Ber. Deutsch. Chem. Ges.* iii. 305.

[3] *Ib.* ix. 320.

into ethyl acetacetate, $CH_3CO.CH_2.CO.OC_2H_5$, in which one hydrogen atom, but no more, can be again replaced by sodium. In the ethers which are obtained by the action of the iodides of the alcohol radicals on these sodium compounds the second atom of hydrogen can be replaced by sodium giving rise to compounds such as $CH_3CO.C(C_2H_5)Na.CO_2C_2H_5$. In this the metal can again be replaced by an alcohol radical. The simple and double acetacetates thus obtained are decomposed by concentrated caustic potash in the following way:

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CXY \\ | \\ CO.OC_2H_5 \end{array} + 2KOH = \begin{array}{l} CH_3 \\ | \\ CO.OK \\ \\ CHXY \\ | \\ CO.OK \end{array} + HO.C_2H_5.$$

In this formula X and Y signify either hydrogen or any alcohol radical, and they yield therefore potassium acetate, the potassium salt of a simple or double substituted acetic acid and alcohol.

By the action of baryta water Ketones are formed:[1]

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CXY \\ | \\ CO.OC_2H_5 \end{array} + Ba(OH)_2 = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHXY \end{array} + HO.C_2H_5 + CO_3Ba.$$

578 *Preparation.* In order to prepare ethyl acetacetate, the following process may be employed:

To one kilo. of pure ethyl acetate contained in a flask provided with a reversed condenser 100 grams of sodium cut into small pieces are at once added when the liquid soon begins to boil. When this ceases it is heated on a water-bath until the metal is completely dissolved. To the still warm liquid mass 550 grams of 50 per cent. acetic acid are then added and the whole well shaken up, the mixture allowed to cool, and then 500cc. of water added when the mass separates into two layers. The upper of these is removed, washed with a little water and distilled in the water-bath, when the larger quantity of unaltered ethyl

[1] *Ann. Chem. Pharm.* clxxxvi. 161, where the history of this subject is fully discussed.

acetate distils over. The residue is then submitted to fractional distillation until the chief portion boils at 175°—185°, and the liquid thus obtained is sufficiently pure for most purposes. By repeated fractional distillation a somewhat purer product boiling at 178°—182° is obtained, but as the ether decomposes slightly on distillation into products which will be afterwards described, a perfectly pure substance cannot be thus obtained. In the most favourable case a yield of 175 grams is obtained.[1] The large excess of ethyl acetate is necessary in order to diminish the decomposition which occurs and by which the yield would be much diminished. The alcohol is removed by shaking the portion passing over below 100° with common salt. The upper layer of liquid is then dried over calcium chloride and purified by distillation, and in this way 350—400 grams of ethyl acetate are recovered.

Ethyl acetacetate is a liquid having a pleasant fruity smell, and boiling with slight decomposition at 181°, its specific gravity at 20° being 1·0256. When brought in contact with sodium amalgam and water it is converted into $\beta$-oxybutyric acid.[2] A very characteristic property of this substance is that it is coloured violet by ferric chloride. A similar coloration is produced by the same reagent in diabetic urine, and for this reason Geuther suggested that this liquid probably contains ethyl acetacetate, and this is rendered more probable by the fact that such urine yields the products of the decomposition of the ether, namely acetone and alcohol. More recent experiments render it almost certain that Geuther's suggestion is correct although the ether has not yet been isolated from this liquid. The quantity present is very small. In one case the amount was determined by converting it into iodoform, and it was found that in eight days 100 parts of urine had yielded from 0.0399 to 0.01909 of ethyl acetacetate, probably occurring in the form of sodium compound.[3]

It has already been stated that ethyl acetacetate decomposes on distillation. In this case a peculiar acid is formed to which Geuther has given the name of *dehydracetic acid*, $C_8H_8O_4$. This is obtained in considerable quantity when the ether is heated for three hours to a temperature of 230°—250°, when a

[1] *Ann. Chem. Pharm.* clxxxvi. 214.
[2] Wislicenus, *ib.* cxlix. 205.
[3] Rupstein, *Fresenius' Zeitsch.* xiv. 419; Hilger, *Ann. Chem. Pharm.* cxcv. 314.

considerable quantity of ethyl acetate together with other products is formed.[1] It is best obtained however by passing ethyl acetacetate through a tube heated below dull redness, when alcohol and acetone are also formed.[2] It is difficulty soluble in cold water but dissolves more readily in hot alcohol and crystallizes in rhombic tables which melt at 108°·5 and boil with partial decomposition at 269°. It is a monobasic acid and does not undergo change when heated with strong sulphuric acid or concentrated nitric acid. If heated with concentrated caustic soda it decomposes into acetone, acetic acid and carbon dioxide. Its constitution is unknown.

## METALLIC COMPOUNDS OF ETHYL ACETACETATE.

579 These contain one atom of hydrogen which is easily replaceable by metals, and this no doubt is rendered possible by the presence of the two carbonyl groups. The salts of acetacetic ether have been chiefly investigated by Geuther and by Conrad.[3]

*Ethyl Sodacctate*, $C_6H_9O_3Na$. This important compound is best obtained in the following way: 10 parts of sodium are dissolved in 100 parts of absolute alcohol and an equal volume of anhydrous ethyl ether added, and then gradually a mixture of 56·5 parts of ethyl acetacetate and the same quantity of anhydrous ether. The mixture is then well shaken with 2 parts of water when the whole is converted into a thick paste consisting of crystalline needles, which are then brought on to a filter pump and dried in a vacuum over sulphuric acid. In this way a glistening, light, white mass is obtained, whilst the filtrate, which still contains some of the compound, is distilled with acetic acid in order to regain the acetacetic acid.[4] Ethyl sodacetacetate crystallizes from hot benzol in feathery needles.

It has already been stated that this substance is employed for the synthesis of various compounds. If the iodide of an alcohol radical act upon this body, sodium is replaced by the radical, and a substituted ethyl acetacetate is obtained, which

[1] Conrad, *Ber. Deutsch. Chem. Ges.* vii. 688.
[2] Oppenheim and Precht, *ib.* ix. 323 and 1099.
[3] *Ann. Chem. Pharm.* clxxxviii. 269.
[4] Harrow, *ib.* cci. 143.

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being decomposed by strong alkalis yields acetic acid, an homologous acid, and alcohol. This substituted ethyl acetacetate again forms a sodium compound in which the metal can be replaced by an alcohol radical, and by the decomposition of the compound thus obtained a doubly substituted ethyl acetate is formed (Part I. p. 181). Less powerful alkalis such as baryta water decompose the ethyl acetacetate into a ketone, carbon dioxide and alcohol. If, instead of an iodide of an alcohol radical, the ethereal salt of an halogen-substituted fatty acid be employed, a class of ethers is obtained which in a similar way yield by the action of alkalis either the acids of the oxalic series or ketonic acids. In the ethereal salts of the latter, finally, another atom of hydrogen may be replaced by sodium, and this again by carbon radicals, and thus the synthesis of the higher dibasic acids and of the tribasic acids may be accomplished.

In most cases it is not necessary to obtain the ethyl sodacetacetate in the pure state, but the process may be carried out as follows. Sodium is dissolved in ten times its weight of absolute alcohol, and to the cold liquid the calculated quantity of acetacetic acid added and then the halogen compound, when a reaction usually occurs spontaneously. This is allowed to go on slowly, but in some cases it must be aided by heat, whilst if it become too rapid the mixture will require cooling or the halogen compound must be added by degrees. The end of the reaction is easily indicated by the fact that the solution no longer renders red litmus-paper blue. The larger quantity of the alcohol is then distilled off on the water bath, water is added to the residue and the lighter layer of liquid purified by fractional distillation. The mono-substituted ether thus obtained treated in the same way yields a doubly substituted one. If, however, the same alcohol radical has to be introduced twice, the same quantity of sodium ethylate solution is added when the reaction is over and then the process carried on as above described. In many cases two atoms of sodium may be introduced into one molecule of ethyl acetacetate at once, and then two molecules of the halogen compound may be added.

If the products of decomposition of the ethyl acetacetate are required and not the pure ether itself, it is simpler to remove the larger quantity of alcohol as above described and treat the residue with alkali.[1]

[1] Conrad and Limpach, *Ann. Chem. Pharm.* cxcii. 153.

When ethyl sodacetacetate is treated with iodine the following reaction takes place :

$$\begin{matrix} CH_3.CO.CHNa.CO.C_2H_5 \\ CH_3.CO.CHNa.CO.C_2H_5 \end{matrix} + I_2 = \begin{matrix} CH_3.CO.CH.CO_2.C_2H_5 \\ | \\ CH_3.CO.CH.CO_2.C_2H_5 \end{matrix} + 2NaI.$$

The diacetosuccinic ether thus obtained is easily soluble in ether and alcohol, and crystallizes in rhombic tables which melt at 77°,[1] and yields a series of interesting products of decomposition, which will be described further on.

580 *Ethyl Magnesium Acetacetate*, $(C_6H_9O_3)_2Mg$, is precipitated by mixing ethyl acetacetate with a solution of magnesium sulphate, ammonia and sal-ammoniac. This may be crystallized from solution in hot benzene or ether in glistening laminæ melting at 240°.

In a similar way the rose-red cobalt compound and the green nickel compound may be obtained. These are also soluble in hot benzene, and crystallize from that solvent.

*Ethyl Copper Acetacetate* $(C_6H_9O_3)_2Cu$, is formed when a solution of copper sulphate in ammonia is shaken with ethyl acetacetate ether. It crystallizes from hot benzene or alcohol in glistening green needles which sublime partially at 178°, melt at 182°, and decompose at a higher temperature with separation of copper.

*Ethyl Aluminium Acetacetate*, $(C_6H_9O_3)_3Al$, separates out when a solution of potassium aluminate is mixed with ethyl acetacetate. Glistening needles are deposited in a few hours and these are soluble in ether and benzene. These melt at 76°, and when gently heated in a narrow sloping tube can be volatilized without decomposition.

Hence the copper and aluminium compounds belong to the small class of organo-metallic bodies containing oxygen which can be volatilized without decomposition. Amongst other compounds possessing this property we find aluminium ethylate, ethyl lead hydroxide, and ethyl tin hydroxide, &c.

581 *Ethyl Chloracetacetate*, $CH_3.CO.CHCl.CO_2.C_2H_5$, is formed when sulphuryl chloride is allowed to drop into ethyl acetacetate :

$$CH_3.CO.CH_2.CO_2.C_2H_5 + SO_2Cl_2 = CH_3.CO.CHCl.CO_2.C_2H_5 + HCl + SO_2.$$

It is a liquid boiling at 193°—195°, and its vapour attacks

[1] Rügheimer, *Ber. Deutsch. Chem. Ges.* vii. 892.

the eyes. Alcoholic potash decomposes the liquid with formation of chloracetic acid.[1] It also forms metallic compounds.[2]

*Ethyl Dichloracetacetate*, $CH_3.CO.CCl_2.CO_2.C_2H_5$, is obtained by acting with chlorine on ethyl acetacetate,[3] as well as by treating it with an excess of sulphuryl chloride. It is a liquid boiling at 205°—207° and having a faint ethereal smell, but the vapours excite a flow of tears. When heated with dilute hydrochloric acid to 170°—180° it decomposes into carbon dioxide, alcohol, and unsymmetrical dichloracetone, $CH_3.CO.CHCl_2$, whilst potash decomposes it into acetic acid and dichloracetic acid.

*Ethyl Nitroso-acetacetate*, $CH_3.CO.CH(NO).CO_2.C_2H_5$, is formed when ethyl acetacetate is dissolved in dilute caustic potash and a quantity of potassium nitrite equivalent to the potash used added, the mixture kept cold and acidified with dilute sulphuric acid, then made alkaline and the yellow solution shaken up with ether. The compound crystallizes from chloroform in colourless glistening hard prisms and dissolves in alkalis with a yellow colour. It melts at 52°—54°, and does not yield Liebermann's reaction with phenol and sulphuric acid (Part I. p. 421) but gives an intense red colouration. Its aqueous solution has an acid reaction.[4]

582 *Ethyl Amido-acetacetate*, $C_6H_{11}NO_2$, is a compound obtained by passing dry ammonia into well-cooled ethyl acetacetate. It is soluble in all proportions in alcohol and ether, and crystallizes in short, thick, monoclinic prisms, which melt readily. They are not soluble in water, but are soon converted in contact with it into a heavy liquid which solidifies at 2°—4°.[5] This body probably has the double molecular weight, and stands to ethyl acetacetate in the same relation as diacetonamine stands to acetone (Part I. p. 574).

*Ethyl Thiocarbacetacetate*, $CH_3.CO.C(CS).CO_2.C_2H_5$, is formed when ethyl acetacetate is heated with carbon disulphide and lead oxide or zinc oxide to 100°. It crystallizes from hot alcohol in small straw-coloured needles melting at about 160°.

*Thiorufic Acid*, $C_{10}H_{14}S_3O_4$. The sodium salt of this acid is produced when the product of the action of sodium on ethyl acetate is treated with carbon disulphide and washed with water. It forms brick-red coloured needles, and the free acid obtained

[1] Allihn, *Ber. Deutsch. Chem. Ges.* xi. 567. [2] *Ib.* xii. 1298.
[3] Conrad, *Liebig's Ann.* clxxxvi. 232.
[4] Meyer and Züblin, *Ber. Deutsch. Chem. Ges.* xi. 320.
[5] Precht, *ib.* xi. 1193.

from these by the action of hydrochloric acid crystallizes in orange-red glistening scales. Its formation takes place in two stages:

$$(1)\ CH_3.CO.CHNa.CO_2.C_2H_5 + CS_2 = CH_3.CO.CH(CS_2Na)CO_2.C_2H_5.$$

The sodium xanthate (Part I. p. 389) which is formed at the same time, acts at once upon the compound which is thus produced[1]:

$$(2)\ CH_3.CO.CH(CS_2Na)CO_2.C_2H_5 = CS\langle^{SNa}_{OC_2H_5} = CH_3.CO.C\langle^{CS.SNa}_{CO.OC_2H_5} - CS.OC_2H_5 + NSH.$$

Sodium acts upon other ethereal acetates as it does upon common ethyl acetate. The following ethereal salts of acetacetic acid have been prepared:

| | | B.P. | Sp. Gr. | At |
|---|---|---|---|---|
| [2] Methyl ether, | $C_4H_5O_3.CH_3$ | 169-170° | 1·037 | 9° |
| [3] Isobutyl ether, | $C_4H_5O_3.C_4H_9$ | 202-206° | 0·979 | 0° |
| [4] Amyl ether, | $C_4H_5O_3.C_5H_{11}$ | 223° | 0·945 | 10° |

Methyl acetacetate is coloured a dark cherry red by ferric chloride; the others do not assume this colouration. They form metallic compounds, and may be distilled with slight decomposition when some hydracetic acid is formed, the alcohol radical not taking part in the reaction (Emmerling and Oppenheim).

[1] Norton and Oppenheim, *Ber. Deutsch. Chem. Ges.* x. 701.
[2] Brandes, *Zeitsch. Chem.* 1668, 454.
[3] Emmerling and Oppenheim, *Ber. Deutsch. Chem. Ges.* ix. 1097.
[4] Conrad, *Ann. Chem. Pharm.* clxxxvi. 228.

# THE SUCCINYL COMPOUNDS.

## SUCCINIC ACID, $C_2H_4(CO_2H)_2$.

583 In his work, *De Natura Fossilium*, published in 1550, Agricola states that on the distillation of amber, which he considers to be an earthy resin, a saline substance is formed together with other bodies. Libavius, in his *Alchymia* (1595), also mentions this body:—"*Flos succini: mistis silicibus, spiritubusque humidis abstractis flos elevatur.*"[1] In the same place he also describes a preparation of amber oil. He says:—"*Summi alembic sal crystalli instar adhaeret.*"

The early accounts respecting the salts of amber, or flowers of amber as it was called, were, however, very contradictory. Obtained from amber by means of heat, it was believed to be a volatile lye-salt; others considered it to be a body composed chiefly of sulphur. Lemery was the first to indicate its true nature. In his *Cours de Chimie* (1679), he says[2]: "*J'ay reconnu que ce sel etoit acide, et semblable à celuy des plantes, qu'on appelle essentiel.*" Other chemists also indicated the acid nature of this body, but the idea that it was a substance similar to the vegetable acids was rejected by many, and it was believed to contain either sulphuric acid or hydrochloric acid. Some held, according to Pott, that the acid of amber-salt is nitric acid, but he showed[3] that this view is incorrect, and that succinic acid is a peculiar substance which most closely resembles the vegetable acids. This was confirmed by Stockar von Neuforn's careful investigation, *Dissertatio de Succino*, published in 1760, and from this time forward succinic acid was considered as one of the proximate constituents of amber, and Bergmann, in 1782, in his *Sciagraphia*, defined it as *petroleum acido succini adamantum*. Its composition was first ascertained by Berzelius.

Succinic acid is found in certain lignites and fossil wood, as well as in amber, and it also frequently occurs in the vegetable

[1] Lib. ii. tract. ii. cap. xl. [2] P. 460.
[3] *Proceedings of the Berlin Academy*, 1753.

kingdom. Its existence has been proved in the lettuce (*Lactuca sativa*, and *L. virosa*), as well as in wormwood (*Artemisia absinthium*), and in the flowers of *A. maritima*, and other wormwoods. It is also found in the poppy (*Papaver somniferum*), in the celandine (*Chelidonium majus*), in *Escholtzia californica*, and probably also in other papavers. Its occurrence in unripe grapes,[1] whilst dioxysuccinic acid or tartaric acid is contained in the ripe fruit, is remarkable. Succinic acid is also found in the animal kingdom, frequently occurring in urine and in blood. It is also found in the sacs of echinococci (hydratids), in the thymoid gland of the calf, as well as in the spleen of the ox.

584 Succinic acid is also a product of several kinds of fermentations. Beissenhirtz long ago stated that it is formed when a mixture of bread, honey, carob beans, vinegar, alcohol, and water is allowed to undergo the acetic fermentation.[2] The truth of this statement has since been frequently denied, but Dessaignes found that many organic acids in the presence of chalk and cheese undergo a fermentation in which succinic acid is formed.[3] It likewise occurs in urine collected after eating plants containing compounds, such as asparagine, malic acid, &c.

It is to Pasteur, however, that we owe the discovery that succinic acid is an essential product of both alcoholic and acetic fermentations, and that it is contained in wine, beer, and vinegar.

Succinic acid is also formed when nitric acid acts upon such bodies as the fatty acids containing four or more atoms of carbon. Butyric acid[4] yields, however, but little, and is chiefly oxidized to water and carbon dioxide. Caproic acid, on the other hand, gives a larger yield, acetic acid being formed at the same time, about half the theoretical quantity being obtained.[5] The higher fatty acids and the fats give homologues of succinic acid, and these then undergo further oxidation. Other derivatives of the paraffins and, indeed, these themselves,[6] are oxidized by nitric acid, with formation of succinic acid.

Succinic acid was first synthetically prepared by Maxwell Simpson,[7] from ethylene, by heating the bromide with potassium cyanide, when succinonitril, $C_2H_4(CN)_2$, is produced, and this yields the acid when heated with a mineral acid or with caustic

[1] Brunner and Brandenburg, *Ber. Deutsch. Chem. Ges.* ix. 982.
[2] *Berlin. Jahrb.* 1818, 158.
[3] *Ann. Chim. Phys.* [3], xxv. 253.
[4] Dessaignes, *Compt. Rend.* xxx. 350.
[5] Erlenmeyer, Sigel, and Belli, *Ann. Chem. Pharm.* clxxx. 207.
[6] Schorlemmer, *ib.* cxlvii. 214.
[7] *Proc. Roy. Soc.* x. 574.

potash. Geuther[1] obtained it at the same time, and by a similar method, from ethylene chloride. It is singular that succinic acid can also be prepared when, instead of the latter compound, its isomeride ethidene chloride, $CH_3.CHCl_2$, is employed.[2] In this case, however, the formation of the nitril does not occur until the temperature of 150° is reached, and hence we may assume that chlorethylene and hydrocyanic acid are first formed, and these unite in the nascent state to form chlorethylene cyanide, $CH_2Cl.CH_2.CN$, which is converted into succinonitril by the potassium cyanide.

Nöldecke obtained succinic acid by treating the product of the action of sodium on ethyl acetate with ethyl chloracetate, and decomposing the substance thus obtained by caustic soda. In accordance with the views which were then prevalent (see p. 170), he believed that the chloracetate united with the hypothetical body sodacetic ether to form ethyl succinate which was then decomposed by caustic soda.[3] Later investigations have, however, shown that the ethyl ether of acetosuccinic acid is first produced, having the following constitution:

$$\begin{array}{l} CH_3.CO.CH.CO_2.C_2H_5 \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad CH_2.CO_2.C_2H_5. \end{array}$$

It is a faintly ethereal smelling liquid, which is converted by the action of strong alkalis into acetic acid, alcohol, and succinic acid.

Succinic acid is also formed by heating $\beta$-iodopropionic acid with potassium cyanide. The $\beta$-cyanopropionic acid thus obtained is boiled with caustic potash.[4] It is likewise formed, though with difficulty, and in smaller quantity, when bromacetic acid is heated with molecular silver.[5]

$$\begin{array}{l} CO.OH \\ | \\ CH_2Br \\ \quad + \quad 2Ag \quad = \\ CH_2Br \\ | \\ CO.OH \end{array} \qquad \begin{array}{l} CO.OH \\ | \\ CH_2 \\ | \quad + \quad 2AgBr. \\ CH_2 \\ | \\ CO.OH \end{array}$$

[1] *Ann. Chem. Pharm.* cxx. 268.
[2] Simpson, *ib.* cxlv. 373; *Comptes Rend.* lxv. 351; Mühlhausen and Erlenmeyer, *ib.* cxlv. 365.
[3] *Ann. Chem Pharm.* cxlix. 224.
[4] Richter, *Zeitsch. Chem.* 1868, 449.
[5] Steiner, *Ber. Deutsch. Chem. Ges.* vii. 184.

585 Succinic acid is prepared by the dry distillation of amber, when, in addition to this body, amber-oil and amber-resin are obtained, the latter remaining in the retort. All these products find employment in the arts (see Amber). The acid is found in the distillate, partly in the solid form, and partly in aqueous solution. The distillate is warmed, filtered hot through a moist filter, and evaporated to crystallization. On cooling, a yellow-coloured crystalline mass is obtained which cannot be perfectly freed from empyreumatic oil by recrystallization. This, however, may be effected by boiling with nitric acid of specific gravity 1·32.

Succinic acid is also easily prepared by the fermentation of crude calcium malate prepared from the berries of the mountain-ash (p. 198). According to Liebig, 4 parts of the malate are mixed with 24 parts of water and 1 part of common yeast, and the mixture allowed to ferment in a tolerably warm place. Another process is to take only half the above quantity of water, to heat it, and to add $\frac{1}{12}$ part of rancid cheese to 1 part of calcium salt.[1] According to Kohl, the yield depends upon the nature and quantity of the ferment, as well as on the temperature at which the fermentation takes place.[2] If this goes on too quickly, and if the temperature rise above 30°, either a small or no yield of succinic acid is obtained, butyric acid and other products being formed. This is due to the presence of foreign ferments, for it has been shown by Fitz, that if small rod-like schizomycetes be added in place of yeast or decomposing cheese, the theoretical yield of acetic and succinic acids is obtained.[3]

Malic acid is oxysuccinic acid, and is decomposed by the *Bacillus* as follows:

$$C_4H_6O_5 + H_2O = C_2H_4O_2 + 2CO_2 + 2H_2,$$

whilst the hydrogen which is liberated reduces another part of the malic acid to succinic acid:

$$C_4H_6O_5 + H_2 = C_4H_6O_4 + H_2O.$$

Succinic acid may also be prepared by the fermentation of tartaric acid. The best yield (about 25 per cent. of the tartaric acid used) is obtained as follows. A solution of 2 kg. of tartaric acid is neutralized with ammonia and diluted to 40 liters, and

[1] *Ann. Chem. Pharm.* lxx. 104 and 363.
[2] *Arch. Pharm.* cxxxiv. 257; cxliii. 12.
[3] *Ber. Deutsch. Chem. Ges.* xi. 1890; xii. 481.

20 grams of potassium phosphate, 10 grams of magnesium sulphate, and a few grams of calcium chloride added. A small quantity of this liquid is diluted to five times its volume, and allowed to stand. After a few days this becomes turbid and swarms with bacteria, and about 20 cc. of it are added to the principal solution, and this kept at a temperature between 25° and 30°, air being excluded as much as possible. After six to eight weeks the tartaric acid has disappeared. The liquid is heated until the ammonium carbonate formed has all volatilized, clarified with white of egg, and boiled with milk of lime until no more ammonia is given off.[1]

The acid is obtained from the slightly soluble calcium salt by decomposing with sulphuric acid. It crystallizes in monoclinic tables or prisms, which have a faintly acid taste, are soluble in 17 parts of water at 17°, and 0·83 part at 100°, and melt at 180°. The fused acid begins to boil at 235°, decomposing to a considerable extent into water and the anhydride. Succinic acid is a very stable body, being but slightly acted on by oxidizing agents even when heated. Its aqueous solution, when exposed to sunlight in presence of a uranic salt decomposes into propionic acid and carbon dioxide.[2] When an aqueous solution of sodium succinate is electrolyzed, hydrogen is obtained at the negative-, and a mixture of carbon dioxide and ethylene at the positive-pole. Oxygen is also found mixed with the two latter gases, and as the operation proceeds, more and more of this gas is formed until at last it alone is evolved.[3]

### The Succinates.

**586** The normal salts of the alkali metals and of magnesium, manganese, and nickel are easily soluble in water, those of the other metals are almost all sparingly soluble or insoluble. Of these, which have been chiefly investigated by Döpping,[4] Fehling,[5] and Handl,[6] the following may be mentioned:

*Ammonium Succinate*, $C_4H_4O_4(NH_4)_2$, can only be obtained in the pure state when its aqueous solution is evaporated in an atmosphere of ammonia. It is deposited in transparent six-sided prisms, which lose ammonia on exposure to air. It is employed

[1] König, *Ber. Deutsch. Chem. Ges.* xv. 172.
[2] Seekamp, *Ann. Chem. Pharm.* cxxxiii. 253.
[3] Kekulé, *ib.* cxxxi. 79. See also Bourgoin, *Ann. Chim. Phys.* [4], xiv. 157.
[4] *Ann. Chem. Pharm.* xlvii. 253. [5] *Ib.* xlix. 158.
[6] *Wien. Akad. Ber.* xxxii. 254.

in quantitative analysis for the separation of iron and manganese, and has been used medicinally.

If a neutral solution of the salt be evaporated in the air, when a certain concentration is reached triclinic prisms are obtained, which consist of the acid ammonium succinate, $C_4H_4O_4(NH_4)H$.

*Calcium Succinate*, $C_4H_4O_4Ca$, is a very characteristic salt of succinic acid. If boiling solutions of sodium succinate and calcium chloride be mixed, fine needles of this salt quickly separate out, containing one molecule of water of crystallization, and if they are allowed to remain in contact with the liquid they take up two molecules more of water. This latter compound is also obtained when the above solutions are mixed in the cold. After some time, needles, which gradually become thicker and harder, are deposited. Calcium succinate occurs in the bark of the mulberry tree (*Morus alba*);[1] it is slightly soluble in water and acetic acid, more readily in a solution of succinic acid, and very easily in nitric acid. From the latter solution the acid salt, $(C_4H_4O_4)_2CaH_2$, is obtained on evaporation. This is also formed when calcium carbonate is treated with a warm solution of succinic acid. It crystallizes in transparent prisms and is decomposed by water and hot alcohol with formation of the normal salt.

*Barium Succinate*, $C_4H_4O_4Ba$, is less soluble than the calcium salt. It is a crystalline precipitate consisting of microscopic tables or prisms. It dissolves in about 250 parts of cold water and is not much more soluble in aqueous succinic acid, though it is tolerably soluble in acetic acid.

*Silver Succinate*, $C_4H_4O_4Ag_2$, is a heavy white precipitate slightly soluble in water and acetic acid, but easily soluble in nitric acid and ammonia.

*Ferric Succinate.* When ferric chloride is added to a solution of a succinate a gelatinous precipitate is obtained, which is at first yellow and becomes darker on standing. This consists of the basic salt, $(C_4H_4O_4)_2Fe_2(OH)_2$. After drying it forms a brick-red powder and when dried at 180° loses one molecule of water. The precipitate is somewhat soluble in cold water and almost insoluble in boiling water,[2] but dissolves in an excess of ferric chloride and easily in acids. At its formation free succinic acid is produced, and for this reason, when it is desired to preci-

[1] Goldschmidt, *Monatsh. Chem.* iii. 136.
[2] S. Young, *Journ. Chem. Soc.* 1880, i. 674.

pitate it completely from its solution, an excess of ferric chloride must be added and the liquid neutralized by ammonia. This compound is easily decomposed by boiling with ammonia.

If a solution of a succinate contains sodium acetate, ferric chloride produces a bright red precipitate, which can be easily washed by alcohol, but becomes gelatinous when brought in contact with water.

Ammonia decomposes these precipitates. If the filtrate be then treated with barium chloride, and alcohol added, a crystalline precipitate of barium succinate is obtained. These reactions are used for the detection of succinic acid and its separation from other acids.

## ETHEREAL SALTS OF SUCCINIC ACID.

587 With the exception of the ethyl salts, the normal succinates are alone known.

*Methyl Succinate*, $C_4H_4O_4(CH_3)_2$, is obtained by passing hydrochloric acid gas into a warm solution of succinic acid in methyl alcohol. It is a crystalline mass melting at 20° and boiling at 198°, and yields a vapour having a specific gravity of 5·29.

*Acid Ethyl Succinate*, or *Ethyl Succinic Acid*, $C_2H_4(CO_2C_2H_5)CO_2H$, is formed by heating succinic anhydride with alcohol, and its barium salt is obtained when the normal ether is heated with the requisite quantity of baryta water. The free acid obtained from this is an easily soluble odourless syrup, which can be distilled without undergoing decomposition.

Most of the ethyl succinates are soluble in water and alcohol. A few crystallize and others form amorphous masses.[1]

*Normal Ethyl Succinate*, $C_2H_4(CO_2C_2H_5)_2$. This body was first prepared in 1835, by Darcet, by distilling a mixture of concentrated hydrochloric acid, succinic acid and alcohol.[2]

Cahours prepared this ether by passing hydrochloric acid gas into a solution of succinic anhydride in absolute alcohol,[3] and Fehling obtained it by passing hydrochloric acid into 95 per cent. alcohol containing succinic acid in solution and suspension.[4]

It is an oily mobile liquid having an aromatic smell and a

[1] Heintz, *Pogg. Ann.* cviii. 70.
[2] *Ann. Chim. Phys.* [2]. lviii. 291.
[3] *Ib.* [3], ix. 206.
[4] *Ann. Chem. Pharm.* xlix. 186.

specific gravity of 1·072. It boils at 217° (Kopp), and the specific gravity of its vapour is 6·2.

As early as 1844 Fehling investigated the action of potassium on this ether, and obtained an oily liquid having the empirical formula, $C_6H_8O_3$. This body when boiled with caustic potash yielded alcohol and succinic acid. Geuther suggested that this substance stands in the same relation to ethyl succinate as his ethyl diacetic acid does to ethyl acetate, and the truth of the hypothesis was shown by Hermann,[1] who proved this *ethyl succinyl-succinate* to have the following constitution :

$$\begin{array}{l} CH_2.CO.CH.CO_2.C_2H_5 \\ | \qquad\qquad | \\ CH_2.CO.CH.CO_2.C_2H_5. \end{array}$$

In order to prepare this body, potassium is gradually added to ethyl succinate, when a violent evolution of hydrogen occurs, and a reddish-brown gummy mass remains. This is then treated with 2 to 3 times its volume of benzene and more potassium added until 1 part of the metal has been employed to every 6 parts of the ether. The product having been freed from benzene as completely as possible by means of the filter-pump, it is decomposed with very dilute hydochloric acid, and the buttery mass thus obtained pressed between filter-paper, washed with cold alcohol, and recrystallized from hot alcohol, then again washed with water and crystallized from ether.

Sodium acts similarly on ethyl succinate but less energetically and much more slowly than potassium, but may nevertheless be used for the preparation of the ether.[2]

Ethyl succinyl-succinate forms triclinic tables or prisms, having a light green colour, and when dissolved in alcohol, ether, or benzene, gives a solution possessing a splendid blue fluorescence. The crystals melt at 127°. Alcoholic potash produces in an alcoholic solution of this body, a white precipitate of the compound, $C_{12}H_{15}KO_6$, which yields with an excess of potash a splendid orange coloured compound, having the composition $C_{12}H_{14}K_2O_6$, the aqueous solution of which has a yellow colour. This solution easily decomposes, but when freshly prepared yields with magnesium salts a purple coloured precipitate of the composition $C_{12}H_{14}MgO_6 + 2H_2O$, a body which at 80° loses water and becomes yellow. The disodium compound, $C_{12}H_{14}Na_2O_6 + 4H_2O$,

[1] *Ber. Deutsch. Chem. Ges.* viii. 1039 ; x. 107 and 646.
[2] Hermann, *Lieb. Ann.* ccxi. 306.

is deposited in fine red microscopic needles; the calcium salt, $C_{12}H_{14}CaO_6 + H_2O$, is obtained as a yellow precipitate.

The yellow potash solution soon decomposes out of contact with the air, forming of the monethyl ether:

$$\begin{array}{l} CH_2.CO.CH.COOH \\ | \quad\quad | \\ CH_2.CO.CH.COOC_2H_5. \end{array}$$

This compound is very difficultly soluble in water and forms a greyish white powder, having a slight acid reaction. It melts at 98° forming carbon dioxide and the ethyl ether of succinyl propionic acid, which has the following composition:

$$\begin{array}{l} CH_2.CO.CH_2 \\ | \quad\quad | \\ CH_2.CO.CH.CO.O.C_2H_5. \end{array}$$

This is an oily liquid having a bitter taste and giving a violet colour with ferric chloride. In presence of air, the alkaline solution undergoes other changes, and bodies belonging to the aromatic series are formed, such, for example, as hydroquinone-dicarboxylic acid, $C_6H_2(OH)_2(CO_2H)_2$.

*Acid Ethylene Succinate*, or *Ethylene Succinic Acid*, $C_2H_4\begin{matrix}O.CO.C_2H_4.CO_2H \\ OH\end{matrix}$, is formed by heating ethylene glycol with succinic acid. It is a colourless liquid which at 300° loses water, forming *ethylene succinate*, $C_2H_4(CO_2)_2C_2H_4$. This body is soluble in water and is deposited from hot alcohol in small crystals which melt at 90°.[1]

*Ethyl Lacto-succinate*, $C_2H_4\begin{matrix}CO_2C_2H_5 \\ CO_2.CH(CH_3)CO_2.C_2H_5\end{matrix}$, is formed when an alcoholic solution of potassium ethyl succinate is heated with ethyl *a*-chlorpropionate. It is an oily liquid, having at 0° a specific gravity of 1·119, and boiling at 280°. It is decomposed by caustic potash into alcohol, succinic acid, and lactic acid.[2]

*Ethyl Succino-lactate*, $C_2H_4\begin{matrix}CO_2.CH(CH_3)CO_2.C_2H_5 \\ CO_2.CH(CH_3)CO_2.C_2H_5\end{matrix}$, is formed by the action of succinyl chloride on ethyl lactate, and is an oily liquid which boils with slight decomposition at 300° —304°.

[1] Lourenço, *Ann. Chem. Pharm.* cxv. 358.
[2] Friedel and Wurtz, *Ann. Chim. Phys.* [3], lxiii. 120.
[3] Wislicenus, *Ann. Chem. Pharm.* cxxxiii. 262.

588 *Succinyl Oxide*, or *Succinic Anhydride*, $(CH_2.CO)_2O$. It has already been stated that succinic acid decomposes on distillation into this compound and water. The products, however, again partially unite on cooling. The addition of phosphorus pentoxide prevents this reunion.[1] It is also formed by heating the acid with phosphorus pentachloride in the proportion of equal molecules:[2]

$$\begin{matrix} CH_2.CO.OH \\ | \\ CH_2.CO.OH \end{matrix} + PCl_5 = \begin{matrix} CH_2.CO\diagdown \\ | \qquad O \\ CH_2.CO\diagup \end{matrix} + 2HCl + POCl_3.$$

It is, however, most easily obtained by distilling equal molecules of succinic acid and succinyl chloride.[3] It crystallizes from hot alcohol in long needles, melting at 118° and boiling at 250°.

*Succinyl Chloride*, $C_2H_4(COCl)_2$, is formed when succinic acid is heated with 2 molecules of phosphorus pentachloride (Gerhardt and Chiozza). It is a highly refracting liquid and possesses a penetrating odour. It boils at 190° with slight decomposition and solidifies at 0° to tabular crystals. Its specific gravity is 1·39.

By the action of zinc ethyl on succinyl chloride *diethyl succinyl* or *diethyl ethylene ketone*, $C_2H_4(CO.C_2H_5)_2$, is produced. This is a liquid insoluble in water, which forms crystalline compounds with the sulphites of the alkaline metals and is decomposed by heat.[4]

## SULPHUR COMPOUNDS OF SUCCINYL.

589 *Thiosuccinic Acid*, $C_2H_4(CO.SH)_2$. This substance is not known in the free state, but its potassium compound is formed when phenyl succinate, a body which will be described under Benzene, is warmed with an alcoholic solution of potassium hydrosulphide:

$$C_2H_4\begin{cases} CO.OC_6H_5 \\ CO.OC_6H_5 \end{cases} + 2HSK = C_2H_4\begin{cases} CO.SK \\ CO.SK \end{cases} + 2HO.C_6H_5.$$

It is very soluble in water and crystallizes in white needles. Hydrochloric acid decomposes it with evolution of sulphuretted

[1] Darcet, *Ann. Chim. Phys.* [2], lviii. 282.
[2] Gerhardt and Chiozza, *Ann. Chem. Pharm.* lxxxvii. 290.
[3] Möller, *Journ. Prakt. Chem.* [2], xxii. 193.
[4] Wischin, *Ann. Chem. Pharm.* cxliii. 262.

hydrogen and formation of succinyl sulphide, $C_2H_4(CO)_2S$, a body crystallizing in a radiating crystalline mass, soluble in water and alcohol, having an acid reaction, and melting at 31°. Its solution gives precipitates with many metallic salts.[1]

*Sulphono-Succinic Acid*, $C_2H_3(SO_3H)(CO_2H)_2$. This strong tribasic acid was obtained by Fehling [2] by passing the vapour of sulphur trioxide over succinic acid. He termed it *succino-sulphurous acid*, a name which was afterwards changed to *succino-sulphuric acid*. The product of the reaction is a brown tenacious mass. This is warmed for some time to 40°—50° and then diluted with water, when on the addition of barium carbonate or white-lead the excess of sulphuric acid is removed, and the filtrate allowed to evaporate in a vacuum. The syrupy liquid which remains slowly deposits warty crystals, which contain 2 molecules of water and absorb moisture from the air.

By the action of succinyl choride on silver sulphate Carius and Kämmerer obtained a compound which on decomposition with water yielded succino-sulphuric acid, a compound which they believed to be isomeric with sulphono-succinic acid.[3] The two bodies are, however, doubtless identical.

## NITROGEN COMPOUNDS OF SUCCINYL.

590 *Succinamide*, $C_2H_4(CO.NH_2)_2$, is formed when ethyl succinate is shaken up in contact with aqueous or alcoholic ammonia. Crystalline needles soon separate out. These are soluble at 19° in 220, and at 100° in 9 parts of water, and are almost insoluble in absolute alcohol and ether. This compound decomposes when melted.[4]

*Succinimide*, $C_2H_4(CO)_2NH$. This body was obtained by Darcet by the action of ammonia on succinic anhydride, and was termed sucinamide.[5] Fehling found later on that it is also formed when ammonia is passed over fused succinic acid or when normal ammonium succinate or succinamide is heated to 200°, and he termed it bisuccinamide. It is also formed, together with platinum ammonium chloride, when an aqueous solution of succinamide is heated with platinic chloride.[6] Its present name was

[1] Weselsky, *Ber. Deutsch. Chem. Ges.* ii. 518.
[2] *Ann. Chem. Pharm.* xxxviii. 285.
[3] *Ib.* cxxxi. 167.
[4] Fehling, *ib.* xlix. 196.
[5] *Ann. Chim. Phys.* [2], lviii. 294.
[6] *Ann. Chem. Pharm.* xlix. 198.

given to it by Laurent and Gerhardt who subjected it to further examination.[1] It is tolerably soluble in water and crystallizes in transparent rhombohedrons or tables which contain one molecule of water and effloresce on exposure to air. At 100° it becomse anhydrous and then melts at 125°—126°.[2] When the anhydrous compound is dissolved in acetone and this allowed to evaporate transparent rhombic pyramids are obtained which are permanent in the air.[3] It boils without decomposition at 288°, but on heating with alcoholic ammonia it is converted into succinamide:

$$\begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>\!NH + NH_3 = \begin{matrix} CH_2.CO.NH_2. \\ | \\ CH_2.CO.NH_2. \end{matrix}$$

Succinimide has an acid reaction and contains one hydrogen atom which can be replaced by certain metals.

*Silver Succinimide*, $C_2H_4(CO)_2NAg$. Siver oxide is dissolved in aqueous succinimide solution and the hot filtrate deposits colourless crystals having the composition $2C_4H_4O_2NAg+H_2O$ and considered by Laurent and Gerhardt to be silver succinamate. They lose water at 100°. The anhydrous compound is also formed when ammonia and silver nitrate are allowed to act on an alcoholic solution of the imide. It crystallizes in prisms and detonates on heating whilst the hydrated compound decomposes quietly. When added to a solution of iodine in absolute alcohol iodo-succinimide, $C_2H_4(CO)_2NI$, is formed, a body crystallizing in hard quadratic prisms, easily soluble in water, less so in alcohol, and decomposes readily in solution (Bunge).

*Mercury Succinimide*, $[C_2H_4(CO)_2N]_2Hg$, is formed by dissolving mercuric oxide in hot aqueous succinimide. It is very soluble in water, somewhat less so in alcohol, and crystallizes in long silky needles.[4]

591 *Succinamic Acid*, $C_2H_4\begin{cases} CO.NH_2 \\ CO.OH \end{cases}$, is formed by the action of bases and water on succinimide.[5] In order to prepare it solutions of baryta and succinimide are warmed, when barium succinamate is deposited in white silky needles. The acid, which is set free by sulphuric acid, is easily soluble in water,

[1] *Compt. Rend. Chim.* 1847, 291.
[2] Erlenmeyer, *Zeitsch. Chem.* 1849, 174.
[3] Bunge, *Ann. Chem. Pharm. Suppl.* vii. 117.
[4] Menschutkin, *ib.* clxii. 165.
[5] Teuchert, *ib.* cxxxiv. 136; Menschutkin, *loc. cit.*

crystallizes in large rectangular tables which have a pleasant acid taste and decomposes at about 300° into succinimide and water. Its salts as a rule crystallize well and their solutions decompose on boiling with formation of ammonia, a decomposition which occurs even in the cold when free alkalis are present.

*Trisuccinamide*, $(C_2H_4O_2)_3N_2$, is formed by the action of silver succinimide on an ethereal solution of succinyl chloride:

$$C_2H_4\begin{matrix}CO.Cl\\CO.Cl\end{matrix} + 2AgN\begin{matrix}CO\\CO\end{matrix}C_2H_4 =$$

$$C_2H_4\begin{matrix}CO.N\begin{matrix}CO\\CO\end{matrix}C_2H_4\\CO.N\begin{matrix}CO\\CO\end{matrix}C_2H_4\end{matrix} + 2AgCl.$$

It crystallizes in small prisms or tables melting at 83° and is decomposed by water into succinic acid and succinimide.[1]

*Succincyanamide*, $C_2H_4\begin{cases}CO.N(CN)H\\CO.N(CN)H\end{cases}$. The potassium compound of this is obtained by the action of potassium cyanamide, N(CN)HK, on ethyl succinate and the sodium compound by heating succinyl chloride with sodium cyanamide. Silver nitrate produces a white precipitate of the silver compound, $C_2H_4(CONAg.CN)_2$, which yields the pure amide on decomposition with sulphuretted hydrogen. This is soluble in water and alcohol, and crystallizes in monoclinic prisms containing two molecules of water which they readily lose. The anhydrous compound melts at 104°—105°.

*Succincyanimide*, $C_2H_4\begin{matrix}CO\\CO\end{matrix}N.CN$, is formed by the action of cyanamide on an ethereal solution of succinyl chloride. It deposits in large crystals insoluble in cold water, which melt at 138° with decomposition and when heated with cyanamide it combines to form the foregoing compound.

*Succincyamic Acid*, $C_2H_4\begin{cases}CO.N(CN)H,\\CO.OH\end{cases}$ is formed when succincyanimide is heated with water. In order to prepare it, succinic anhydride is dissolved in a cold aqueous solution of caustic potash and of cyanamide:

$$C_2H_4\begin{matrix}CO\\CO\end{matrix}O + N\begin{matrix}H\\CN\\K\end{matrix} + KOH = C_2H_4\begin{matrix}CO.N\begin{matrix}CN\\K\end{matrix}\\CO.OK\end{matrix} + H_2O.$$

[1] Gerhardt and Chiozza, *Ann. Chim. Phys.* [3], xlvi. 162.

The potassium succincyamate thus obtained is soluble in water but not in alcohol, and it crystallizes in rhombic tables. It forms with silver nitrate a soluble silver compound, from which other succincyamates can be obtained by decomposition with soluble chlorides. If the silver salt be decomposed by sulphuretted hydrogen the free acid is obtained. This compound is easily soluble in water and alcohol, possesses a sharp saline and acid taste and crystallizes in lancet-shaped needles or tables which melt at 128° and decompose at a higher temperature. Its aqueous solution decomposes easily into succinic acid and cyanamide or dicyanamide. Its salts also decompose in a similar way, but less rapidly.

When silver nitrate is added to a concentrated solution of the acid, oily drops separate out and these soon solidify to small rhombic prisms of the acid silver succincyamate, $C_2H_4\begin{cases} CO.N(CN)Ag.^1 \\ CO.OH \end{cases}$

592 *Succinonitril* or *Ethylene Cyanide*, $C_2H_4(CN)_2$, is obtained by heating ethylene bromide with potassium cyanide and alcohol [2] and is also formed in the electrolysis of cyanacetic acid (see p. 159). It forms a white amorphous mass, soluble in water and alcohol, melting at 54°·5 and may, under diminished pressure, be distilled without decomposition. When heated with caustic potash, hydrochloric acid, or nitric acid, it is converted into succinic acid.

*β-Cyanpropionic Acid*, $C_2H_4(CN)CO_2H$, was obtained by von Richter on boiling β-iodopropionic acid with potassium cyanide solution. He did not, however, obtain it in the pure state, and only noticed that the potassium salt thus obtained does not crystallize and that it is converted into potassium succinate on boiling with caustic potash.[3]

An acid of the same composition was obtained by Cooper and Wanklyn by heating woollen yarn with an alkaline solution of potassium permanganate. It is an amorphous yellow mass which softens at 100° and at 140° becomes anhydrous, decomposing at a higher temperature. It is easily soluble in water and alcohol, has a strongly acid reaction and forms amorphous salts, most of which are soluble in water but not in alcohol. When heated with caustic potash to 200°—220°, oxalic acid and

[1] Möller, *Journ. Prakt. Chem.* [2], xxii. 193.
[2] Maxwell Simpson, *Proc. Roy. Soc.* x. 574; Nevolé and Tscherniak, *Bull. Soc. Chim.* [2], xxx. 108 and 161.
[3] *Zeitsch. Chem* 1868, 449.

ethylamine are obtained but no succinic acid. For this reason Cooper and Wanklyn termed it isocyanpropionic acid.[1] Further investigation is required in order to determine the constitution of this body.

## SUBSTITUTION PRODUCTS OF SUCCINIC ACID.

593 *Monobromsuccinic Acid*, $C_2H_3Br(CO_2H)_2$, was obtained by Kekulé by heating succinic acid with water and bromine.[2] According to Carius it is best obtained by heating 5 grams of succinic acid, 2·5 cbc. of bromine and 40 cbc. water slowly to 120°.[3] It forms small colourless octohedral crystals or crusts which melt at 159°—160° undergoing loss of hydrobromic acid. It is soluble in 5 parts of water at 15°. This compound is more readily obtained by the union of hydrobromic acid with fumaric or maleic acid (p. 210).

*Dibromsuccinic Acid*, $(CHBr)_2(CO.OH)_2$, was obtained by Perkin and Duppa by heating equal volumes of succinyl chloride and bromine at 120°—130° and decomposing with water the dibromsuccinyl chloride, $C_2H_2Br_2(COCl)_2$, thus produced.[4] Kekulé also prepared it by heating 12 grams of succinic acid with11 cc. of bromine and 12 cc. of water at 150°—180°.[5] When one molecule of ethyl succinate is heated with two molecules of bromine at 130°—140° ethyl bromide is obtained together with a small quantity of succinic acid, a large quantity of monobromsuccinic acid, and a somewhat smaller quantity of dibromsuccinic acid, which two latter may easily be separated by recrystallization.[6] Dibromsuccinic acid forms large glistening crystals difficultly soluble in cold water, and decomposing at 200° with formation of hydrobromic acid, and brom-maleic acid.

Other substitution products of succinic acid will be considered under fumaric and maleic acids.

[1] *Phil. Mag.* [5], vii. 356.
[2] *Ann. Chem. Pharm.* cxvii. 125; cxxx. 21; *Suppl.* i. 129.
[3] *Ann. Chem. Pharm.* cxx. 6.
[4] *Quart. Journ. Chem. Soc.* xiii. 102.
[5] *Ann. Chem. Pharm.* cxvii. 120; *Suppl.* i. 351. See also Bourgoin, *Bull. Soc. Chem.* xix. 148.
[6] Schacherl, *Ber. Deutsch. Chem. Ges.* xiv. 637.

## ISOSUCCINYL COMPOUNDS.

594 *Isosuccinic Acid* or *Methyl Malonic Acid*, $CH_3.CH(CO_2H)_2$, was first obtained by H. Müller by heating the ethyl ether of *a*-chlorpropionic acid with potassium cyanide and decomposing the product with caustic potash.[1] He considered this to be common succinic acid, but Wichelhaus showed that it was an isomeride.[2] It was then further examined by him and Eller,[3] by v. Richter,[4] and by Byk.[5] In order to prepare it, one part of ethyl *a*-chlorpropionate is gently boiled with two parts of pure potassium cyanide and four parts of water, until the ether is dissolved, the whole neutralised with sulphuric acid and evaporated to dryness. The residue is strongly acidified and extracted with ether, and the cyanpropionic acid thus obtained boiled with potash. Cyanpropionic acid may be advantageously prepared from brompropionic acid.[6] The product is again acidified, extracted with ether, and then precipitated with lead acetate, care being taken not to use an excess, as lead isosuccinate is soluble in the reagent, but only slightly so in acetic acid. The acid obtained from the lead salt forms colourless crystals, dissolving in five parts of cold water. When carefully heated below 100° between watch glasses it can be sublimed in microscopic tables. At a higher temperature decomposition takes place. It melts at 130° and decomposes, when more strongly heated, into carbon dioxide and propionic acid. The salts are mostly crystallizable, are more soluble than those of succinic acid, and are not precipitated by ferric chloride.

*Calcium Isosuccinate*, $C_4H_4O_4Ca+H_2O$, is obtained as a crystalline precipitate formed at once in hot solution and gradually in the cold by mixing calcium chloride solution with a concentrated solution of an alkaline isosuccinate.

*Silver Isosuccinate*, $C_4H_4O_4Ag_2$, is a granular crystalline precipitate, which when shaken with a large quantity of water suddenly dissolves, separating out again, on standing for a few minutes, in thin needles.[7]

[1] *Ann. Chem. Pharm.* cxxxi. 350.
[2] *Zeitsch. Chem.* [2], iii. 247.
[3] *Ber. Deutsch. Chem. Ges.* i. 98.
[4] *Zeitsch. Chem.* 1868, 449.
[5] *Journ. Prakt. Chem.* [2], i. 19.
[6] Rosieki, *Ber. Deutsch. Chem. Ges.* xiii. 209.
[7] Krestownikow, *ib.* x. 409.

*Ethyl Isosuccinate*, $C_4H_4O_4(C_2H_5)_2$, is formed according to Carstanjen by heating ethyl formate and ethyl lactate with phosphorus pentoxide:[1]

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CO.OC_2H_5 \end{array} + HCO.OC_2H_5 = \begin{array}{l} CH \\ | \\ CH.CO.OC_2H \\ | \\ CO.OC_2H_5 \end{array} + H_2O.$$

It is also formed from ethyl malonate by a reaction which has already been described.[2] It is a liquid having a specific gravity of 1·021 at 22° and boils at 196°.[3]

*Monobromisosuccinic Acid.* $CH_3CBr(CO_2H)_2$, is obtained by heating isosuccinic acid with bromine and water to 100°. It crystallizes in well-formed deliquescent prisms.

## OXYSUCCINIC ACIDS.

### Malic Acid, $C_2H_3(OH)(CO_2H)_2$.

595 Geber supposed that the juice of sour pears contained an acid, or, as he termed it, *aqua dissolutiva*, and this liquid was employed in the sixteenth century as a solvent for iron. The preparation thus obtained is still described in certain pharmacopœias as *Extractum martis pomata* or *ferri pomata*, a tincture prepared from this being also mentioned. Libavius, who refers to this in his Alchymia, also notices a juice from "*laccae ericae bacciferae* (*Mehlbehr vocant Germani*), *Succus evadit ruber et acidum qui sapit.*"

Donald Monro, in 1767,[4] was the first to point out that the juice of apples yields a peculiar salt with soda, and Scheele, in 1785, showed that gooseberries contain another acid in addition to citric acid, which is also present in large quantity in unripe apples, and hence he termed it malic acid (from *malum*). He also showed that either the one or the other, or both these acids occur in many other plants, and its characteristic properties were afterwards more closely investigated by Vauquelin in 1800. In 1807, however, both Bouillon-Lagrange and A. Vogel came to the conclusion that this acid is a mixture of acetic acid and

[1] *Ber. Deutsch. Chem. Ges.* iv. 868. [2] Züblin, *ib.* xii. 1112.
[3] Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 202.
[4] *Phil. Trans.* 1767, p. 479.

extractive matter, but this was disproved by Vauquelin in 1817. Two years before Donovan proved that mountain-ash berries contained an acid to which he gave the name of *sorbic acid*, and Braconnot, in 1818, proved this substance to be malic acid. The exact composition of malic acid was, however, first ascertained by Liebig.[1]

Malic acid is widely distributed throughout the vegetable kingdom,[2] being found in a number of other fruits besides those which have been named. It frequently occurs together with oxalic, tartaric and citric acids, partly in the free state and partly combined with bases. It also occurs in various other parts of the vegetable kingdom. For example it is found in considerable quantity in the berries of berbery (*Berberis vulgaris*), quince, red- and white-currants, raspberries, blackberries, pine-apple, bananas, and sour- or morella-cherries, whilst sweet cherries contain acid potassium malate, a salt which is also contained in the leaves and stem of garden rhubarb (*Rheum palmatum* and *R. undulatum*). Acid calcium malate is also found in many plants, the leaves of the house-leek (*Sempervivum tectorum*) being especially rich in it, as well as the leaf of the tobacco plant and the berries of *Rhus Coriaria*, and other species of sumach.

The best source of malic acid is the mountain-ash berries. They must be used when they begin to redden, as the ripe ones contain little or no malic acid. Milk of lime is added to the juice until the liquid has only a slightly acid reaction. The whole is then boiled for some hours, when the steam which comes off attacks the eyes from the presence of the vapour of sorbic acid. During the ebullition calcium malate separates out as a white sandy powder, which is then removed with a spoon. When no further precipitate forms, the liquid is allowed to cool and a further quantity of this salt is deposited. The precipitate is then washed with cold water and thrown gradually into a warm mixture of nitric acid and ten parts of water so long as it dissolves, and the whole allowed to cool, when the acid calcium malate separates out. This is then purified by recrystallization from hot water, precipitated with lead acetate and the insoluble lead malate decomposed with sulphuretted hydrogen.[3]

The stalks and leaves of garden rhubarb may also be employed for the preparation of malic acid, and may be treated as above.[4]

[1] *Ann. Pharm.* v. 141. [2] Gmelin, *Handbook*, x. 205.
[3] Hagen, *Ann. Chem. Pharm.* xxxviii. 257.
[4] Everitt. *Phil. Mag.* [3], xxiii. 327.

The juice may also be clarified with isinglass and the filtrate allowed to evaporate to a thin syrup. After some days acid calcium malate separates out, and this may be purified by recrystallization and afterwards treated as above.[1]

The evaporated syrupy solution from the decomposition of the lead salt when allowed to stand in a warm place deposits malic acid in glistening four-sided needles, which frequently unite to form bushy or nodular masses. It is also sometimes deposited in cauliflower-like forms.

Malic acid is very soluble in water, and deliquesces on exposure to moist air. It has a strong but pleasant acid taste, melts at about 100°, and decomposes at a higher temperature, when products are formed which will be afterwards described. When treated with concentrated hydriodic acid it is reduced to succinic acid :[2]

$$C_2H_3(OH)(CO_2H)_2 + 2HI = C_2H_4(CO_2H)_2 + H_2O + I_2.$$

## The Malates.

596 These salts have been carefully investigated by Hagen.[3] The normal malates of the alkali metals are easily soluble in water, but do not crystallize. The acid salts on the other hand crystallize well. The malates of the alkaline earths exist both in anhydrous forms and in forms containing water of crystallization, and it appears that the solubility increases with the quantity of water contained. The malates of aluminium, iron, manganese, &c., are not crystallizable, and their solutions are not precipitated by alkalis. Other heavy metals form difficultly soluble or insoluble malates. The following are the most characteristic salts of this acid.

*Acid Ammonium Malate*, $C_4H_5O_5(NH_4)$, dissolves in about three parts of cold water, and crystallizes in large rhombic prisms.

*Normal Calcium Malate*, $C_4H_4O_5Ca$. When a solution of malic acid is neutralized with lime and heated to the boiling point, the anhydrous salt separates out as a granular powder scarcely soluble in water. When the solution remains acid a similar precipitate is thrown down which contains one molecule of

[1] Winkler and Herberger, *Jrb. Prakt. Chem.* ii. 201.
[2] Schmitt, *Ann. Chem. Pharm.* cxiv. 106; Dessaignes, *ib.* cxvii. 134.
[3] *Loc. cit.*

water, and this is also formed when a solution of sodium malate is mixed with one of calcium chloride and allowed to stand. This salt is soluble in 147 parts of cold and 67 parts of boiling water, and does not deposit again on cooling. If the acid is neutralized with lime water and the solution allowed to evaporate in a vacuum easily soluble thin crystalline laminæ are obtained, containing two molecules of water. These become anhydrous and insoluble at 180°.

*Acid Calcium Malate*, $(C_4H_5O_5)_2Ca + 8H_2O$. This occurs, as has been stated, in several plants, and may also be easily prepared by dissolving the normal salt in aqueous malic acid or in hot dilute nitric acid. It crystallizes in transparent glistening prisms having a pleasant acid taste. It dissolves in fifty parts of cold and more easily in hot water. When its solution is boiled the normal salt separates out, and when neutralized with ammonia and allowed to evaporate transparent brightly glistening, hard crystals are deposited, having the composition $C_4H_4O_5Ca + 3H_2O$, and these, when heated, lose water and assume a porcelain-like appearance.

*Normal Lead Malate*, $C_4H_4O_5Pb + 3H_2O$. This is obtained as a flocculent precipitate which gradually becomes crystalline. When heated with a moderate amount of water it melts to a gum-like mass which is brittle when cold. The solution, however, deposits four-sided needles or tablets. It is only slightly soluble in dilute acetic acid, but dissolves more readily in solution of sugar of lead and in nitric acid. When a solution of a malate is thrown down with acetate of lead a precipitate of basic salt is obtained.

*Silver Malate* is a white granular crystalline precipitate soluble in boiling water, and easily undergoes decomposition attended by blackening.

## Optical Isomerides of Malic Acid.

597 The malic acid which occurs in nature is optically active, a dilute solution deviating the plane of polarization to the left. This gyratory power diminishes with the concentration until, when the solution contains thirty-four per cent., it becomes inactive. A still further addition of the acid gives to the solution a dextro-rotatory power, so that one containing sixty per cent. deviates the plane of polarization as much

to the right as one containing 8·4 per cent. does to the left. The sodium salts exhibit a similar property.[1]

When tartaric acid (dioxysuccinic acid) is treated with hydriodic acid it is reduced to malic acid, and this by a further action is converted into succinic acid. The malic acid thus obtained is, like the tartaric acid employed, dextro-rotatory at any rate in dilute solution.[2] If instead of tartaric acid use be made of its isomeride, racemic acid, a compound of dextro-tartaric acid with lævro-rotatory acid which is optically inactive, an inactive malic acid is also produced, and this, like racemic acid, can be decomposed into two optically active acids.[3] Another inactive malic acid which cannot be thus split up was obtained by Pasteur by the action of nitrogen trioxide on inactive aspartic acid (amidosuccinic acid), a body which will be afterwards described. This malic acid is distinguished from the common variety by being more easily crystallizable, by being non-deliquescent, and melting at 133°.[4] Its salts are, however, very similar to those of the naturally occurring acid, but they may be distinguished from them inasmuch as the crystals of the latter exhibit hemihedral faces. It is probable that the malic acid obtained by Kekulé by heating bromsuccinic acid with silver oxide and water[5] is identical with Pasteur's acid as well as that which Strecker and Messel obtained by boiling sulphosuccinic acid with caustic potash.[6] Another inactive malic acid which appears to be different from these modifications is obtained from fumaric acid, $C_4H_4O_4$, and will be described under this head.

## Ethers and Ethereal Salts of Malic Acid.

598 *Normal Ethyl Malate*, $C_2H_3(OH)(CO_2C_2H_5)_2$. Thenard[7] made the first experiments on the preparation of this salt. He heated a mixture of eighteen parts of alcohol, fifteen parts of sulphuric acid, and five of malic acid until ether began to be evolved, and then mixed the residue with water, when he obtained a yellow oily odourless liquid, which when heated decomposed. This substance requires further investigation.[8] According to

[1] Schneider, *Ann. Chem. Pharm.* ccvii. 257.
[2] Bremer, *Ber. Deutsch. Chem. Ges.* viii. 1594.
[3] Bremer, *ib.* xiii. 351.
[4] *Ann. Chem. Pharm.* lxxxiv. 157.
[5] *Ib.* cxvii. 125.
[6] *Zeitsch. Chem.* 1870, 460.
[7] *Mém. Soc. d'Accueil*, ii. 12.
[8] Gmelin, *Org. Chem.* ii. 354.

Demondésir this salt is obtained by saturating an alcoholic solution of malic acid with hydrochloric acid. The acid is then neutralized with carbonate of soda, and extracted with ether, and on evaporating ethyl malate remains behind.[1] It is also formed when silver malate is heated with ethyl iodide and ether. It is a slightly ethereal smelling liquid, soluble in water, and boiling under a diminished pressure of 15 mm. at 128°—131°. When heated under the ordinary pressure it decomposes into water and ethyl fumarate.

*Acid Ethyl Malate*, $C_2H_3(OH)(CO_2C_2H_5)CO_2H$. This compound, which is also known as ethyl malic acid, is formed in the preparation of the normal salt by the second method above described, and forms a calcium salt easily soluble in alcohol.

*Ethylomalic Acid*, $C_2H_3(OC_2H_5)(CO_2H)_2$, is isomeric with the foregoing compound, being distinguished from it inasmuch as it is dibasic. In order to prepare it, ethyl fumarate is gradually added to an alcoholic solution of sodium ethylate, the mixture allowed to stand, and then heated with water and caustic soda. The sodium salt thus obtained is then converted into the insoluble and crystalline lead salt, and this decomposed by sulphuretted hydrogen. When the solution is evaporated a syrupy mass remains behind, which gradually deposits crystals which are apparently rhombic, and melt at 86°. The formation of this acid is explained by the following equation:

$$C_2H_5.CO_2.CH \equiv CH.CO_2.C_2H_5 + NaOC_2H_5 = C_2H_5.CO_2.CH(OC_2H_5).CHNa.CO_2.C_2H_5.$$

The compound thus obtained is then converted in the presence of water and caustic soda into sodium ethylomalate.[2]

*Triethyl Malate*, $C_2H_3(OC_2H_5)(CO_2C_2H_5)_2$, is formed when sodium is gradually added to an ethereal solution of the normal ether, and the product treated with ethyl iodide. It is a liquid which boils under a diminished pressure of 15 mm. at 118°—120°.[3]

*Ethyl Nitroxyl Malate*, $C_2H_3(ONO_2)(CO_2C_2H_5)_2$, is obtained by dissolving the normal salt in a mixture of concentrated sulphuric and nitric acids. On precipitating with water, a slightly pungent-smelling, oily liquid is obtained, which decomposes on heating.[4]

[1] *Compt. Rend.* xxxiii. 227. [2] Purdie, *Journ. Chem. Soc.* 1881, i. 344.
[3] Andreoni, *Ber. Deutsch. Chem. Ges.* xiii. 1394. [4] Henry, *ib.* iii. 532.

*Ethyl Acetomalate,* $C_2H_3(OC_2H_3O)(CO_2C_2H_5)_2$, is formed by heating ethyl malate with acetyl chloride. It is a heavy, slightly ethereal smelling liquid, insoluble in water, boiling at 258°, and is decomposed by alkalis into alcohol, malic acid, and acetic acid.[1]

### Amido-compounds of Malic Acid.

599 *Malamide,* $C_2H_3(OH)(CO.NH_2)_2$, is formed by the action of ammonia on an alcoholic solution of ethyl malate. It is soluble in water and crystallizes in quadratic prisms.

*Malamic Acid,* $C_2H_3(OH)\begin{cases} CO.NH_2 \\ CO.OH \end{cases}$, is not known in the free state. Its ethyl salt separates out as a radiating crystalline mass when ethyl malate is saturated with ammonia and allowed to stand (Demondésir).

*Asparagine,* or *Amidosuccinamic Acid,* $C_2H_3(NH_2)\begin{cases} CO.NH_2 \\ CO.OH \end{cases}$

This compound, isomeric with malamide, was discovered in 1805 by Vauquelin and Robiquet in the juice of asparagus.[2] Bacon found a substance in the marsh-mallow root to which he gave the name of *Althäine,* and Caventou found in the liquorice root a similar body, which he termed *Agèdoile.* Plisson and Henry then showed that these bodies are identical with asparagine.[3] The composition of this body was first determined by Liebig.[4] It occurs, very widely distributed, in the vegetable kingdom, being found in certain fruits, roots, and tubers, as in the dahlia tuber, and in chestnuts and potatoes, and in the roots of *Robinia pseudacacia,* in which it occurs in comparatively large quantities. It is also found in the milky juice of the lettuce, and in the young shoots of vetches, peas, beans, and several other leguminous plants, the seeds of which do not contain any trace. The quantity diminishes as the growth of the plants proceeds, and disappears altogether as soon as the seeds are formed.[5] According to Boussingault, asparagine is a constant constituent of plants grown in the dark.[6]

In order to prepare it from the young plants these are pressed, the juice heated to boiling, filtered and evaporated to a thin

[1] Wislicenus, *Ann. Chem. Pharm.* cxxix. 179.
[2] *Ann. Chim.* lvii. 88; lxxii. 143.
[3] *Ann. Chim. Phys.* [2], xxxv. 175; xxxvii. 81; xlv. 304.
[4] *Ann. Pharm.* vii. 146.
[5] Piria, *Ann. Chim. Phys.* [3], xxii. 160.
[6] *Bull. Soc. Chim.* [2], ii. 297.

syrup. After standing for some time asparagine separates out, and this is then purified by filtration through animal charcoal and crystallization. It may be prepared easily from the root of *Scorzonera hispanica*, by allowing this to undergo dialysis,[1] and a similar process may also be adopted for its preparation from the mallow.[2]

Asparagine crystallizes with one molecule of water in transparent rhombic prisms, which are permanent in the air, and have a specific gravity of 1·519. These crumble to powder with a crackling noise between the teeth; they have a slight cooling, somewhat nauseating taste. They are soluble in 82 parts of water at 10°, but are scarcely soluble in absolute alcohol.

The aqueous solution possesses a slight lævro-rotatory power; that in ammonia or caustic soda exerts a more powerful action, but a solution in mineral acids has a dextro-gyratory power. The effect of acetic acid upon this action is remarkable. If a small quantity be added to an aqueous solution of asparagine its lævro-rotatory power is weakened, and at last disappears, a further addition of acetic acid producing a dextro-rotatory action.[3]

Asparagine being an amido-acid combines with acids. It also forms metallic salts, and combines with salts to form compounds similar to those formed by glycocoll.

Nitrous acid converts asparagine into malic acid, and for this reason Piria assumed that this body stands in the same relation to this as oxamide does to oxalic acid. Kolbe, on the other hand, was the first to express the view that it is an amide of amido-succinic acid or aspartic acid,[4] and Schaal proved this, inasmuch as he obtained it by the action of ammonia on the ethyl salt of the latter acid.[5]

Pure asparagine does not undergo alteration in aqueous solution. If, however, albuminoid bodies are present a fermentation soon sets in, and ammonium succinate is formed. This change occurs in its passage through the human organism. After eating asparagus the urine, as is well known, assumes a peculiar smell. The cause of this has not yet been ascertained, but on examination it has been found that such urine contains ammonium succinate.[6]

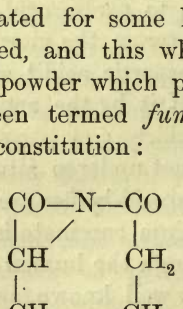
600 *Aspartic Acid* or *Amidosuccinic Acid*, $C_2H_3(NH_2)(CO_2H)_2$

[1] Gorup-Besanez, *Ann. Chem. Pharm.* cxxv. 291.
[2] Buchner, *Zeitsch. Chem.* 1862, 117.
[3] Becker, *Ber. Deutsch. Chem. Ges.* xiv. 1028.
[4] *Ann. Chem. Pharm.* cxxi. 232.
[5] *Ib.* clvii. 24.
[6] Hilger, *Ib.* clxxi. 209.

was obtained by Plisson by boiling asparagus with water and lead oxide until the evolution of ammonia ceased. Instead of lead oxide, other bases such as baryta,[1] or caustic potash [2] may be used. Liebig, who first determined its composition, prepared it by boiling an aqueous solution of asparagine with caustic potash, the evaporated water being constantly renewed, until no further evolution of ammonia was observed. The solution was then neutralized with hydrochloric acid, evaporated to dryness, and the residue washed with cold water to remove potassium chloride. Aspartic acid is also found in beet-root juice after treatment with lime,[3] as well as in the spent lees or vinasse, together with an homologous acid.[4]

It is sparingly soluble in cold water, more readily soluble in boiling water, and dissolves only with difficulty in alcohol. It is deposited either in small thin rhombic tables or in microscopic crystals. These have a slightly acid taste, leaving an after-taste like broth. Owing to the slight solubility its aqueous solution possesses only a weak lævro-rotatory power, whilst its alkaline solution produces a more powerful rotation; its solution in acids, on the other hand, exhibits a strong dextro-rotatory action. With acetic acid it exhibits a behaviour corresponding to that of asparagine (Becker).

An optically inactive aspartic acid was obtained by Pasteur [5] from acid ammonium malate. If this body be moistened with ammonia and heated for some hours to 160°—200°, a resinous mass is formed, and this when washed with water leaves behind a reddish powder which possesses the composition $C_4H_3NO_2$, and has been termed *fumarimide*. It probably possesses the following constitution:

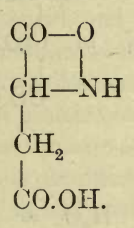


By boiling this with dilute hydrochloric acid it is converted

[1] Boutron-Chalard and Pelouze, *Ann. Chim. Phys.* [2], lii. 90.
[2] Liebig, *Ann. Pharm.* xxvi. 125 and 161.
[3] Scheibler, *Jahresb.* 1866, 399; *Chem. Centralb.* 1869, 509.
[4] *Ber. Deutsch. Chem. Ges.* ii. 596.
[5] *Ann. Chim. Phys.* [3], xxxiv. 30.

into inactive aspartic acid, which crystallizes in short hard monoclinic prisms, and is somewhat more soluble than the active acid. Its salts also exhibit a difference from those of the active acid both in solubility and crystalline form; otherwise its chemical reactions resemble those of the ordinary acid.[1]

Aspartic acid has a slightly acid taste and is dibasic. Its normal salts are, however, decomposed by carbon dioxide, and hence they were at one time believed to be basic salts, and the acid was considered to be monobasic, as, indeed, in the free state it really is, being an amido-acid:



The only aspartates of the alkali metals which are known in the solid form are the acid salts. The acid salts of other metals are soluble in water; some of the normal salts are insoluble. The soluble aspartates have also a peculiar taste like broth. By heating the acid silver salt with ethyl iodide the monethyl salt is obtained; this is a crystalline body, which on treatment with aqueous ammonia yields asparagine.[2]

Aspartic acid also forms compounds with other acids which are crystalline.

*Imidosuccinic Acid*, $\left\langle \begin{matrix} CO \\ NH \end{matrix} \right\rangle C_2H_3.CO_2H$, is obtained together with tetramethylammonium iodide when a solution of asparagine in caustic potash is mixed with wood-spirit and methyl iodide, and the mixture allowed to stand. It crystallizes from hot water in four-sided laminæ. It is a monobasic acid, but as it is an imido-compound it yields a silver salt containing two atoms of metal.[3]

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601 *Isomalic Acid*, $CH_3C(OH)(CO_2H)_2$, was obtained by Schmöger by gently heating an aqueous solution of bromisosuccinic acid with freshly precipitated silver oxide. This acid, which is easily soluble in water, can be obtained in the crystallized state,

[1] *Ann. Chim. Phys.* [3], xxii. 160.
[2] Schaal, *Ann. Chem. Pharm.* clvii. 24.
[3] Griess, *Ber. Deutsch. Chem. Ges.* xii. 2117

whereas its salts, with the exception of the silver salt, cannot be obtained crystallized. It decomposes at 100° into carbon dioxide and lactic acid.[1]

An acid, which according to its mode of formation should be identical with the above, was prepared by Böttinger in the following way. Pyroracemic acid is gradually added to finely powdered, well cooled potassium cyanide, and the product treated with hydrochloric acid, when *oxyethidene-succinamic acid* is formed:

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CO.OH \end{array} + HCN = \begin{array}{l} CH_3 \\ | \\ C(OH)CN \\ | \\ CO.OH. \end{array}$$

$$\begin{array}{l} CH_3 \\ | \\ C(OH)CN \\ | \\ CO.OH \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ C(OH)CO.NH_2 \\ | \\ CO.OH. \end{array}$$

This forms a strongly acid syrupy mass, which when heated with hydrochloric acid is converted into lactic acid, carbon dioxide, and sal-ammoniac, but when boiled with baryta water, *oxyethidene-succinic acid*, or *methyl tartronic acid* is formed. This is easily soluble, and crystallizes in rhombohedrons similar to those of calc-spar. When carefully heated it melts at 178° with violent evolution of carbon dioxide. It is distinguished from isomalic acid, inasmuch as it forms crystalline salts.[2]

## FUMARIC ACID AND MALEIC ACID, $C_4H_4O_4$.

602 Vauquelin[3] as well as Braconnot[4] noticed that when malic acid is subjected to dry distillation an acid aqueous liquid first comes over, and then a needle-shaped sublimate is formed. Lassaigne then showed that the aqueous solution contains a peculiar acid to which he gave the name of pyromalic acid, the sublimate being an acid differing from this.[5] These compounds were more accurately examined in 1834 by Pelouze, who gave to

[1] *Journ. Prakt. Chem.* [2], xiv. 77; xix. 168; xxiv. 38.
[2] *Ber. Deutsch. Chem. Ges.* xiv. 87 and 148.
[3] *Ann. Chim. Phys.* [2], vi. 337. [4] *Ib.* viii. 149. [5] *Ib.* ix. 93.

the former the name of maleic acid and to the latter the name of paramaleic acid.[1]

Before this, Braconnot had prepared the so-called boletic acid from several varieties of lichens, and Pfaff afterwards found an acid in Iceland-moss to which he gave the name of lichenic acid, whilst Winkler obtained an acid from fumitory (*Fumaria officinalis*), which he termed fumaric acid. The identity of this latter acid with paramaleic acid was demonstrated by Demarçay,[2] whilst Schödler showed that lichenic is really the same acid.[3] Then Bolley[4] and Dessaignes[5] proved that boletic acid is identical with fumaric acid, and this name is now generally adopted instead of paramaleic acid.

When malic acid is quickly distilled, water passes over first alone and then together with maleic acid, the residue solidifying after some time to crystalline fumaric acid. On slow distillation more of the latter substance is obtained, and when malic acid is heated for some time to 140° to 150°, only fumaric acid is formed, the maleic acid being also converted at this temperature into the isomeride. At higher temperatures, on the other hand, both acids decompose into water and maleic anhydride, which body easily combines with water to form maleic acid. Hence these two isomerides can easily be converted the one into the other.

## Fumaric Acid.

603 Fumaric acid is somewhat widely distributed throughout the vegetable kingdom. It is found in a variety of lichens, and especially in Iceland moss, in truffles, and in the several species of *fumaria*, *corydalis* and *glaucium*.

In addition to the reactions mentioned above it is also formed, according to Mühlhaüser, when albuminoids are heated with aqua regia.[6] It is best obtained in the pure state by heating malic acid with a small quantity of water at 180° under pressure.[7] It requires for solution more than 200 times its weight of cold water. It dissolves more easily in hot water and also in alcohol and ether, crystallizing from these in prisms or scales. It fuses with difficulty on heating, and decomposes at about 200°

[1] *Ann. Chim. Phys.* [2], lvi. 72.
[2] *Ib.* lvi. 429.
[3] *Ann. Chem. Pharm.* xvii. 148.
[4] *Ib.* lxxxvi. 44.
[5] *Compt. Rend.* xxxi. 432 ; xxxvii. 782.
[6] *Ann. Chem. Pharm.* ci. 176.
[7] Jungfleisch, *Bull. Soc. Chim.* xxx. 147.

into water and maleic anhydride, whilst a portion sublimes in needles. It has a purely acid taste, is optically inactive, and is not attacked by concentrated nitric acid, even on boiling; but is easily converted in presence of sodium amalgam and water into succinic acid. This same change takes place when it is treated with zinc in alkaline solution, or when it is heated with hydriodic acid.[1] When brought in contact with bromine and water it combines, gradually at the ordinary temperature but quickly at 100°, forming dibromsuccinic acid.[2] Fuming hydrobromic acid does not combine with it in the cold but does so at 100° when monobromsuccinic acid is formed.[3] When heated with a large excess of water to 150° it is transformed into inactive malic acid (Jungfleisch). This also takes place on heating fumaric acid for some time with caustic soda to 100°. Malic acid prepared in this way forms hard crystalline crusts consisting of microscopic prisms. It is less deliquescent than common malic acid, from which it is also distinguished by the properties of its salts. The main distinction between this and the other modifications of malic acid is that when heated it forms fumaric acid, but no maleic acid.[4]

If, on the other hand, fumaric acid be heated with much water at 150° to 200° an inactive malic acid is formed, which, like the body already described, splits up into maleic anhydride and fumaric acid when it is heated with water. By converting this latter into malic acid and repeating the above reaction, malic acid can be completely converted into maleic acid.[5]

When either fumaric acid[6] or maleic acid[7] is distilled with phosphorus pentachloride *fumaryl chloride*, $C_2H_2(COCl)_2$, is obtained. This is a mobile liquid boiling at 160°, and uniting with bromine to form *dibromsuccinyl chloride*, $C_2H_2Br_2(COCl)_2$, a body which is also formed by heating succinyl chloride with bromine.

A galvanic current passed through an alkaline solution of fumaric acid decomposes it into acetylene, carbon dioxide and hydrogen, which latter body reduces a portion of the acid to succinic acid[8]

[1] Kekulé, *Ann. Chem. Pharm.* Suppl. i. 129.
[2] Kekulé; Fittig and Petri, *ib.* cxcv. 56.
[3] Fittig and Dorn, *ib.* clxxxviii. 87.
[4] Linnemann and Loydl, *Ann. Chem. Pharm.* cxcii. 82.
[5] Pictet, *Ber. Deutsch. Chem. Ges.* xiv. 2648.
[6] Kekulé, *Ann. Chem. Pharm.* Suppl. ii. 86.
[7] Perkin and Duppa, *ib.* cxii. 24.
[8] Kekulé, *Ann. Chem. Pharm.* cxxxi. 84.

Fumaric acid is a powerful dibasic acid. Most of its salts are soluble in water, and ferric chloride produces in solutions of its normal salts a cinnamon-brown precipitate. The normal and acid fumarates of the alkali metals crystallize easily. Those of the alkaline-earth metals are not very soluble in water, and are obtained in crystals when hot concentrated solutions of the corresponding acetates are mixed with a solution of fumaric acid.

*Lead Fumarate*, $C_4H_2O_4Pb+2H_2O$, is slightly soluble in cold and more soluble in hot water and crystallizes in needles.

*Silver Fumarate*, $C_4H_2O_4Ag_2$, is so slightly soluble in water that the solution of the acid in 200,000 parts of water is rendered milky by silver nitrate. In more concentrated solutions it is obtained as an amorphous precipitate, which in the dry state deflagrates on heating, like gunpowder.

*Normal Ethyl Fumarate*, $C_4H_2O_4(C_2H_5)_2$, was obtained by Hagen when endeavouring to prepare the corresponding salt of malic acid. For this purpose he passed hydrochloric acid gas into a solution of malic acid in absolute alcohol and distilled the product. He then also prepared it in a similar way from fumaric acid.[1] Perkin and Duppa obtained the same compound by acting with alcohol on the fumaryl chloride obtained from malic acid, and Henry prepared it by distilling ethyl malate with phosphorus pentachloride.[2] This salt is also formed when fumaric is heated to 120° with absolute alcohol,[3] as also by the action of ethyl iodide on silver fumarate.[4] It is a slightly smelling liquid boiling at 218°·5 and having a specific gravity at 17°·5 of 1·0522, that of its vapour being 5·92.[5] Ethyl fumarate unites readily with bromine to form ethyl dibromsuccinate. It decomposes with ammonia forming *fumaramide*, $C_2H_2(CO.NH_2)_2$, a body forming glistening scales insoluble in cold water and alcohol.

*Acid Ethyl Fumarate*, or *Ethyl Fumaric Acid*, $C_4H_2O_3(C_2H_5)OH$, is formed together with the normal salt by the methods described by Hagen and Laubenheimer. It is deposited in laminea which possess a fatty feel, are difficultly soluble in cold water, and fuse when gently heated (Laubenheimer).

*Methyl Fumarate*, $C_4H_2O_4(CH_3)_2$, forms colourless crystals

[1] *Ann. Chem. Pharm.* xxxviii. 274.
[2] *Ib.* clvi. 177.
[3] Laubenheimer, *Ann. Chem. Pharm.* clxiv. 294.
[4] Anschütz, *Ber. Deutsch. Chem. Ges.* xii. 2280.
[5] Hübner and Schreiber, *Zeitsch. Chem.* 1871, 712.

which are difficultly soluble in cold but dissolve easily in hot water, and volatilize in a current of steam, producing a pleasant smell. It melts at 102° and boils at 192° (Anschütz).

## Maleic Acid.

604 This is not found ready formed in the vegetable kingdom. It was, however, formerly supposed to occur in *Equisetum fluviatile;* but afterwards the acid found in these plants was shown to be its polymeride aconitic acid, $C_6H_6O_6$. Maleic acid crystallizes in rhombic prisms, is very easily soluble in water, and also dissolves in alcohol and ether. Its taste is sour at first, but soon excites an unpleasant sensation of nausea. It melts at about 130°, and the liquid solidifies if kept for some time at this temperature, fumaric acid being formed, a change which also occurs when it is boiled with mineral acids. It behaves like fumaric acid with nascent hydrogen and hydriodic acid, and also yields the same products on electrolysis (Kekulé). It is distinguished from fumaric acid, inasmuch as it is attacked by fuming hydrobromic acid in the cold, being then converted into equal molecules of monobromsuccinic acid and fumaric acid (Fittig and Dorn). Its action with bromine is similar, inasmuch as a part is converted into fumaric acid, some of which again unites with bromine to form dibromsuccinic acid. Another portion of the maleic acid, however, combines directly with bromine to form *isodibromsuccinic acid,* $C_2H_2Br_2(CO_2H)_2$, a body easily soluble in water and crystallizing in scales melting at 160°, and decomposing into hydrobromic and isobrommaleic acids (Kekulé; Fittig and Petri).

*The Maleates.* Most of the maleates are soluble in water and are not precipitated by ferric chloride. The normal maleates of the alkali metals crystallize with difficulty. The acid ones, which and less soluble, crystallize more readily. Those of the metals of the alkaline-earths are somewhat soluble in cold water, the most insoluble being *barium maleate,* $C_4H_2O_4Ba+2H_2O$, crystallizing in shining needles united in stellated groups. Maleic acid gives with baryta water a granular precipitate, which after some time is converted into crystalline scales (Lassaigne ; Pelouze). The acid salts are easily soluble and crystallizable.

*Lead Maleate,* $C_4H_2O_4Pb+3H_2O$. Maleic acid gives a precipitate with solution of sugar of lead, which soon changes into shining micaceous laminæ.

*Normal Silver Maleate*, $C_4H_2O_4Ag_2$, forms a white amorphous precipitate which changes in a few hours to tolerably large transparent colourless crystals having an adamantine lustre. These detonate slightly on application of a gentle heat.

*Acid Silver Maleate*, $C_4H_3O_4Ag$, is obtained in fine colourless needles on mixing not too dilute solutions of maleic acid and nitrate of silver.[1]

*Methyl Maleate*, $C_4H_2O_4(CH_3)_2$, is obtained by the action of methyl iodide on silver maleate. It is a pleasantly smelling liquid boiling at 205°.

*Ethyl Maleate*, $C_4H_2O_4(C_2H_5)_2$, is prepared in a similar way and boils at 225°.

When these ethereal salts are heated with a small quantity of iodine they are converted into the corresponding salts of fumaric acid, and hence it is necessary in their preparation to employ the iodides in a perfectly pure state. Bromine vapour acts in the same way, and they combine with an excess of bromine to form salts of dibromsuccinic acid.

605 *Maleyl Oxide* or *Maleic Anhydride*, $C_4H_2O_3$, is best obtained as follows. Maleic acid is subjected to dry distillation until the residue solidifies; the distillate is then evaporated to dryness and the crude maleic acid thus obtained, together with fumaric acid, is treated with acetyl chloride:

$$C_4H_4O_4 + C_2H_3OCl = C_4H_2O_3 + C_2H_3O.OH + HCl.$$

The product is purified by recrystallization from chloroform (Anschütz).

According to Perkin it is also easily formed when malic acid is treated with acetyl chloride and the whole distilled, when the excess of acetyl chloride first comes over and next the acetic acid which is formed in the reaction. It is also formed by the action of silver fumarate on fumaryl chloride.[2] It crystallizes in needle-shaped prisms melting at 53° and boiling at 202°. Its vapour has a specific gravity of 3·40.[3] It passes easily by absorption of water into maleic acid and combines with bromine to form *isodibromsuccinic anhydride*, $C_4H_2Br_2O_3$ (Kekulé).

In order to prepare this latter body, pure maleic anhydride is dissolved in anhydrous chloroform and heated with the

[1] Anschütz, *Ber. Deutsch. Chem. Ges.* xii. 2280.

[2] *Chem. Soc. Journ.* 1881, i. 559. See also Anschütz, *Ber. Deutsch. Chem. Ges.* xiv. 2791.

[3] Hübner and Schreiber, *Zeitsch. Chem.* 1871, 712.

calculated quantity of bromine to 100°. After removing the chloroform, a yellow oil remains, and this after a time, deposits tabular crystals melting at 32°. This body absorbs moisture from the air with the greatest avidity, and on addition of water to it violent ebullition takes place, isodibromsuccinic acid being formed and this is the best way of preparing this substance in a pure state.[1]

*Brommaleic Acid*, $C_4H_3BrO_4$, is formed by boiling dibromsuccinic acid with water. It forms large transparent crystals melting at 128°. By the action of water and sodium amalgam it is first converted into fumaric acid.

*Isobrommaleic Acid* is obtained in the same way from isodibromsuccinic acid. It crystallizes in large tablets melting at 177°—178° and behaving with sodium amalgam like the foregoing compound. Both acids yield on distillation *brommaleic anhydride*, $C_4HBrO_3$. This is an oily liquid boiling at about 212° and easily combining with water to form brommaleic acid. This latter compound combines quickly in the cold with fuming hydrobromic acid to form dibromsuccinic acid, and at the same time a portion is converted into isobrommaleic acid, whilst the latter combines with hydrobromic acid only slowly in the cold but quickly when heated, to form both the dibromsuccinic acids. This reaction shows that isobrommaleic acid is *bromfumaric acid* (Fittig and Petri).

This last substance combines only slowly, whilst brommaleic acid unites quickly, with bromine to form *tribromsuccinic acid*, $C_2HBr_3(CO_2H)_2$, a body extremely soluble in water and crystallizing in short bushy needles, melting at 136°—137° and being readily deliquescent. When heated with water it decomposes into carbon dioxide, hydrobromic acid and dibromacrylic acid, $C_2HBr_2.CO_2H$ (Petri and Fittig).

606 *Constitution of Fumaric and Maleic Acids.* After having shown that both these acids combine with hydrogen to form succinic acid, but that they yield two isomeric dibromsuccinic acids when they unite with bromine, Kekulé discussed their probable constitution, and arrived at the conclusion that they are unsaturated compounds containing free combining units situated at different positions in the molecule, thus causing their isomerism.[2] But we are now aware, as will be explained under tartaric acid, that dibromsuccinic acid possesses the

[1] Pictet, *Ber. Deutsch. Chem. Ges.* xiii. 1669.
[2] *Ann. Chem. Pharm.* Suppl. ii. 111.

constitution $CO_2H.CHBr.CHBr.CO_2H$ and hence the constitution of the two acids must be represented as follows:

| Fumaric Acid. | Maleic Acid. |
|---|---|
| $-CH.CO_2H$ | $=C.CO_2H$ |
| $\vert$ | $\vert$ |
| $-CH.CO_2H.$ | $CH_2.CO_2H.$ |

Kekulé and Swarts afterwards supported the view that fumaric acid is a saturated compound, the two carbon atoms being connected by two combining units with one another, whilst in maleic acid the existence of free combining units must be assumed.[1]

In the same way Kekulé explained other cases of isomerism and assumed that carbon atoms which unite directly with hydrogen or with the elements of the chlorine group, &c., either contain carbon atoms doubly or trebly linked, or that they contain free combining units.

The latter view was afterwards rejected by most chemists as the constitution of such compounds can be explained without this assumption. According to this, the constitution of the two acids will be as follows:

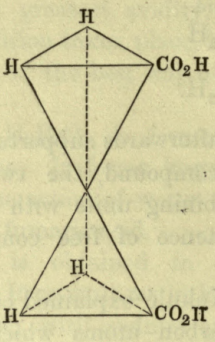
| Fumaric Acid. | Maleic Acid. |
|---|---|
| $CH.CO_2H$ | $CH_2$ |
| $\Vert$ | $\Vert$ |
| $CH.CO_2H.$ | $C(CO_2H)_2.$ |

Many weighty reasons may, however, be cited against the above formula for maleic acid, especially the fact that these two acids are so readily convertible the one into the other. Besides, if maleic acid contain two carboxyls combined with one carbon atom it could not yield an anhydride on heating, but must, like isobutyric acid and similar acids, decompose into carbon dioxide and monobasic acrylic acid, and when it combines with hydrogen give rise to isosuccinic acid.

Another hypothesis of considerable probability has been propounded by Van't Hoff. According to this, the isomerism cannot be explained by the ordinary graphical formulæ because these represent the atoms as arranged in one plane instead of in space.[2] If we imagine the four combining units of a carbon atom forming the corners of a tetrahedron in whose centre the atom

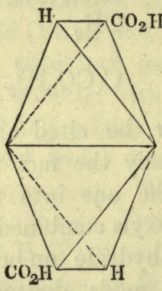
[1] *Zeitschrift. Chem.* [2], iii. 654.
[2] *Lagerung der Atome in Raume.*

is situated, we then obtain the following glyptic formula for succinic acid :

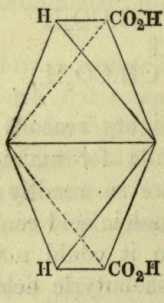



In this no cases of isomerism can occur. If the atoms of hydrogen or the carboxyls which are combined with one of the carbon atoms are arranged in another way, we obtain the above figure again by turning the tetrahedron. If, however, two atoms of hydrogen be withdrawn from succinic acid the two following isomeric acids are possible :

Fumaric Acid.




Maleic Acid.




Fittig, who, with his pupils, has investigated these acids very completely, comes, however, to the conclusion that maleic acid contains free combining units and gives the following formulæ :

Fumaric Acid.

$$\begin{matrix} CH.CO_2H \\ \| \\ CH.CO_2H. \end{matrix}$$

Maleic Acid.

$$\begin{matrix} CH_2.CO_2H \\ | \\ =C.CO_2H. \end{matrix}$$

The varying reactions of bromine, hydrobromic acid, &c., can thus be explained in a simple way, as well as the fact that

dibromsuccinic is converted into brommaleic acid by the separation of hydrobromic acid, whilst isodibromsuccinic acid on the other hand is converted into bromfumaric acid as is shown as follows :[1]

Dibromsuccinic Acid.

$$\begin{array}{l} CHBr.CO_2H \\ | \\ CHBr.CO_2H. \end{array}$$

Isodibromsuccinic Acid.

$$\begin{array}{l} CH_2.CO_2H \\ | \\ CBr_2.CO_2H. \end{array}$$

Brommaleic Acid.

$$\begin{array}{l} CHBr.CO_2H \\ | \\ \equiv C.CO_2H. \end{array}$$

Bromfumaric Acid.

$$\begin{array}{l} CH.CO_2H \\ \| \\ CBr.CO_2H. \end{array}$$

## DIOXYSUCCINIC ACID, OR TARTARIC ACID,

$$C_2H_2(OH)_2(CO_2H)_2.$$

607 The substance known under the name of cream of tartar, gradually deposited from grape-juice on standing, is the acid potassium salt of common tartaric acid. The existence of this subject was noticed by the Greeks, who termed it τρύξ, or wine-lees, and it was known to the Romans as *faex vini*, the latter people being acquainted with the mode of preparing an alkali from it by ignition. The alchemists of the eleventh century termed it *tartarum*, or afterwards *tartarus*, an expression derived from the Arabic *tartir*, a word which is used to designate not only the powder deposited by wine, but also that formed on the teeth. This word "tartarus" was afterwards used in several senses. Paracelsus gave to it two distinct interpretations; in the first place he signified by this the cause of the diseases of the kidney and liver, gout or stone, in which sediments or concretionary masses are deposited, in the same sort of way that tartar separates out from wine. In the second place, however, the term was applied to the pains produced by the disease, resembling the torments of the condemned in Tartarus. Geber gave to the juice of wine containing cream of tartar in solution the name, like other acids, of *aqua dissolvens*, or *aqua dissolvata*, and compared it in this respect to vinegar, and so for a long time cream of tartar was supposed to be a true acid. Thus in the Prussian Pharmacopœia of 1781,

[1] *Ann. Chem. Pharm.* clxxxviii. 95; cxcv. 56.

purified cream of tartar was designated *acidum tartari.* It was not believed that this salt itself contained the alkali, but rather that the alkali was produced in the act of burning, although Kunkel, in 1677, had shown that cream of tartar can be converted into an alkali by boiling it with lime, its earthy constituents being rendered insoluble. Similar observations were made by Duhamel and Grosse, in 1732, who believed that the potassium tartrate, formed at the same time, was tartrate of lime. Marggraf, in 1764, then showed that cream of tartar contains an alkali, but he did not determine what combines with the lime when the salt is boiled with this alkaline-earth. Scheele, in 1769, was the first to ascertain this point and to obtain tartaric acid by decomposing its insoluble lime salt with sulphuric acid, and it is to him we owe the first satisfactory investigation of this acid and its salts. The results of his experiments were communicated to Bergman in order that he might lay them before the Stockholm Academy. This, however, through carelessness he failed to do, and in consequence Scheele wrote the Memoir again, handing it over to the secretary of the Academy, Retzius. At his request it was then printed, in 1770, but it was so edited that much of the credit of the research apparently belonged to Retzius.[1] This was Scheele's first scientific paper, and, owing to the part Bergman took in this matter, Scheele for some time declined to make his acquaintance. This feeling, however, soon gave place to more amicable relations, and eventually they became fast friends. Soon after Scheele's discovery, tartaric acid was manufactured on a large scale.

Professor John of Berlin described in his *Dictionary of Chemistry,* published in 1819, a new "Säure aus den Voghesen," which came into commerce as oxalic acid, and which he at first believed to be a mixture of oxalic and tartaric acids, but afterwards found that it consisted of a single acid closely resembling, and yet distinctly different from tartaric acid. When on a subsequent occasion Gay-Lussac passed through Thann in the Voges, he obtained some of this acid from the manufacturer Kestner, this having been obtained in the years 1822—1824 as a by-product in the preparation of tartaric acid. In 1826 on his return to Paris Gay-Lussac investigated this, and found that it was a peculiar substance, "its stochiometrical number agreeing however within a few thousandths with that of tartaric acid."[2]

[1] *Abh. Schwed. Akad. Wissensch.* 1770, 207; *Crell. Chem. Journ.* ii. 179.
[2] *Schweigg. Journ.* xlviii. 381.

At the same time Walchner occupied himself with the investigation of the same body,[1] to which Gmelin, in 1829, gave the name of racemic acid (Traubensaüre), and soon afterwards Berzelius showed that it possesses the same composition as tartaric acid, and this was the first instance of the introduction of the idea of isomerism into the science.[2] Biot then showed that tartaric acid and racemic acid act optically differently, for whilst the aqueous solution of the first rotates the plane of polarized light to the right, the latter is altogether inactive.[3] This was shown by Pasteur to be due to the fact that racemic acid is a compound of equal molecules of common tartaric acid and another acid which deviates the plane of polarized light as much to the left as the first one does to the right.[4] He also showed that another inactive tartaric acid exists which is distinguished from racemic acid, inasmuch as it cannot be decomposed into two optically active modifications, and he, as well as other chemists, further proved that the various tartaric acids may be converted the one into the other. This matter will be further discussed hereafter.

The modifications of tartaric acid are also formed in the oxidation, by nitric acid,of various kinds of sugars and other carbohydrates (*see* Sugars).

608 *Synthetical Production of Tartaric Acid.* Tartaric acid may be obtained synthetically by several processes. (1) When the silver salt of dibromsuccinic acid is boiled with water the following reaction takes place :

$$\begin{array}{l} CO_2Ag \\ | \\ CHBr \\ | \\ CHBr \\ | \\ CO_2Ag \end{array} + 2H_2O = \begin{array}{l} CO_2H \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO_2H \end{array} + 2AgBr.$$

Instead of the above reaction the calcium salt may be boiled with lime water.[5]

The acid obtained from dibromsuccinic acid is a mixture of racemic acid and inactive tartaric acid or mesotartaric acid.[6]

[1] *Schweigg. Journ.* xlix. 238. [2] *Pogg. Ann.* xix. 319.
[3] *Ann. Chim. Phys.* [2], lxix. 27.
[4] *Ib.* [2], xxiv. 442 ; xxviii. 56 ; *Comptes Rendus*, xxxvi. 26 ; xxxvii. 162 ; see also *Pog. Ann.* lxxx. 127 ; xc. 498, 504.
[5] Kekulé, *Ann. Chem. Pharm.* cxvii. 124; Suppl. i. 375 ; Perkin and Duppa, *ib.* cxvii. 130.
[6] Pasteur, *Ib.* Suppl. ii. 242 ; Jungfleisch, *Bull. Soc. Chim.* [2], xix. 198.

Conversely tartaric acid when treated with hydriodic acid is converted into the corresponding modification of malic acid, and afterwards reduced to succinic acid.

(2) An acid is obtained very similar to racemic acid by boiling oxalaldehyde (glyoxal) with hydrocyanic acid and hydrochloric acid,[1] but this acid is not capable of being decomposed into dextro- and lævro-rotatory acid.[2] Its mode of formation is similar to that of lactic acid from aldehyde, and is represented thus:

$$\begin{matrix}\mathrm{COH}\\|\\\mathrm{COH}\end{matrix} + 2\mathrm{CNH} + 2\mathrm{HCl} + 4\mathrm{H_2O} = \begin{matrix}\mathrm{CO.OH}\\|\\\mathrm{CH.OH}\\|\\\mathrm{CH.OH}\\|\\\mathrm{CO.OH}\end{matrix} + 2\mathrm{NH_4Cl}.$$

(3) It has already been stated that an acid probably identical with the foregoing is formed together with glycollic acid, when an alcoholic solution of ethyl oxalate is treated with sodium amalgam.[3] In this way ethyl glyoxylate is doubtless formed to begin with:

$$\begin{matrix}\mathrm{CO.OC_2H_5}\\|\\\mathrm{CO.OC_2H_5}\end{matrix} + \mathrm{H_2} = \begin{matrix}\mathrm{COH}\\|\\\mathrm{CO.OC_2H_5}\end{matrix} + \mathrm{HO.C_2H_5}.$$

A part of this then combines with hydrogen to form ethyl glycolate, but another part taking up only one atom of hydrogen forms the unsaturated molecule, $\mathrm{CH(OH)CO.OC_2H_5}$, two of which combine together to form ethyl tartrate. This reaction is of great importance as carbon dioxide is easily converted into oxalic acid, and this in a simple way into glycollic and tartaric acids, these two latter occurring together in plants, as for example in the turnip, grape, and in the leaves of the Virginian creeper.

[1] Strecker, *Zeitsch. Chem.* 1868, 216.
[2] Städel, *Ber. Deutsch. Chem. Ges.* xi. 1752.
[3] Debus, *Journ. Chem. Soc.* xxv. 365.

## COMMON, OR DEXTRO-ROTATORY, TARTARIC ACID.

609 This acid is widely distributed in the vegetable kingdom, occurring in the free state or in the form of a salt, especially as acid potassium tartrate, in various fruits, frequently together with malic acid. It is found in the berries of the mountain-ash, the berries of the sumachs, in tamarinds, in mulberries, pine apples, &c. It also occurs in the sap of the vine, and in large quantities in the juice of the grape. Wine produced from the latter source gradually deposits crude argol in crystalline crusts, and this consists chiefly of acid potassium tartrate, but also contains calcium tartrate and the corresponding salts of the isomeride, racemic acid. Its presence has also been detected in potatoes, cucumbers, *chelidonium majus*, quassia, Iceland-moss, black-pepper, madder-root, &c.

Argol is always used for the preparation of tartaric acid, the method being almost exactly that originally proposed by Scheele, but more accurately described by Klaproth.[1] Respecting the manufacture Wurtz gives the following particulars.[2]

From 500 to 700 kilograms of crude argol are brought into a large vat nearly filled up with water and the whole heated with steam to the boiling point, and then chalk powder added until almost neutral. The calcium tartrate is then filtered off, and the solution precipitated with calcium chloride. Gypsum may also be employed instead of chalk; it of course acts more slowly, but decomposes the potassium tartrate after lapse of a few hours. Calcium tartrate prepared according to one of these processes is then washed with water and decomposed by an excess of sulphuric acid, the whole being heated by steam up to 75°. The solution is concentrated in leaden pans and allowed to cool, when the crystals separate out, and these are dried in a centrifugal machine. Fresh crops are obtained on concentrating the mother-liquor, until it becomes too impure, when it is worked up again as raw material. In order to purify the crude acid it is dissolved in warm water and decolourized by addition of animal charcoal, the whole

[1] *Diss. de sale essentiali tartari*, Göttingen, 1779.
[2] *Chem. Centralb.* 1871, 713; *Ber. Entw. Chem. Ind.* ii. 418.

filtered, a small quantity of sulphuric acid added, and the solution concentrated to the point of crystallization. Wooden vessels are used, generally covered with a lining of lead. The addition of sulphuric acid improves the form and size of the crystals as required for market. The crystals always contain small quantities of lead and sulphuric acid. For pharmaceutical purposes they are purified by recrystallization from hot water.

Another raw material employed for the preparation of tartaric acid is the wine-lees left behind in the distillation of brandy. This is heated with dilute hydrochloric acid, allowed to deposit, the clear liquid poured off, and the whole neutralized with lime, when calcium tartrate falls down and is worked up in the way above described.

610 *Properties.* Tartaric acid crystallizes in large transparent monoclinic prisms, having a specific gravity of 1·764. These, like sugar, become luminous when rubbed in the dark, and they possess a strong purely acid taste. 100 parts of water at 15° dissolve 138 parts of the acid, and it is still more soluble in hot water. It is also readily soluble in alcohol; 100 parts of absolute alcohol at 15° dissolve 20·385 parts of the acid, whilst dilute alcohol dissolves it the more readily the weaker it is. On the other hand it is only slightly soluble in ether, 100 parts of the liquid dissolving at 15° only 0·393 part.[1]

It has already been stated that aqueous solutions of tartaric acid deviate the ray of polarized light to the right. Mineral acids diminish this rotatory power, and its solutions in wood-spirit, alcohol, and acetone, exert only a weak dextro-action, whilst a solution in anhydrous ether or acetone is slightly lævro-gyratory.[2]

Tartaric acid melts at 135°, first passing into its isomeride metatartaric acid, and this when more strongly heated yields with loss of water an anhydride-like compound. These bodies will be afterwards described. When tartaric acid is subjected to dry distillation, acetic acid, pyroracemic acids, $C_3H_4O_3$, pyrotartaric acid, $C_5H_8O_4$, and pyrotritartaric acid, $C_7H_8O_3$, are formed. In addition to these, carbon monoxide, carbon dioxide, aldehyde, formic acid, acetone, &c., are formed, and also in very small quantity *dipyrotetracetone* $C_8H_{12}O_2$, an aromatic smelling liquid which boils at 230°.[3]

[1] Bourgoin, *Bull. Soc. Chim.* [2], xxix. 244.
[2] Landolt, *Ber. Deutsch. Chem. Ges.* xiii. 2329.
[3] Bourgoin, *Bull. Soc. Chim.* [2], xxix. 309.

When tartaric acid is treated with phosphorus pentachloride *chlormaleyl chloride* is formed:

$$CH_2(OH)_2(CO.OH)_2 + 4PCl_5 = C_2HCl(COCl)_2 + 4POCl_3 + 5HCl.$$

This is a heavy oily liquid decomposed by water into *chlormaleic acid*, $C_2HCl(CO_2H)_2$, a body crystallizing in easily soluble needles.[1]

Most oxidizing agents convert tartaric acid into formic acid. Thus if 5 parts of the well-dried acid be triturated with 16 parts of lead dioxide the mass becomes incandescent, and carbon dioxide is evolved, having a smell of formic acid.[2] When tartaric acid is boiled with potash or ammonia and silver oxide, the latter is reduced, with formation of carbon dioxide and oxalic acid.[3] In dilute solution it also reduces the chlorides of gold and platinum and precipitates calomel from solutions of corrosive sublimate.

If tartaric acid be fused with caustic potash, acetic and oxalic acids are formed, and when electrolyzed it yields hydrogen, carbon dioxide, and acetic acid.[4]

Tartaric acid is used in medicine, in the processes of dyeing and calico printing, in photography, &c.

## THE TARTRATES.

611 Tartaric acid is a strong dibasic acid and therefore forms a large number of salts, which have been very carefully investigated.[5] Besides the acid and normal salts containing the same metal, many are known containing two different metals, and also a few so-called basic salts in which the hydrogen of the alcoholic hydroxyls are also replaced by metals. Tartaric acid also forms with antimony and other triad elements, a class of peculiar compounds whose constitution will be discussed hereafter. The tartrates are, like tartaric acid itself, dextrorotatory.

[1] Perkin and Duppa, *Phil. Mag.* [4], xvii. 280.
[2] Walker, *Pogg. Ann.* v. 536; Böttger, *Journ. Prakt. Chem.* viii. 477 (or 497).
[3] Erdmann, *Ann. Pharm.* xxi. 14; Claus, *Ber. Deutsch. Chem. Ges.* viii. 950.
[4] Kekulé, *Ann. Chem. Pharm.* cxxxi. 88; Bourgoin, *Bull. Soc. Chim.* [2], xi. 405.
[5] Dulk, *Ann. Pharm.* ii. 39; Berzelius, *ib.* xxx. 88; xxxi. 28; Knapp, xxxii. 76; Werther, *ib.* lii. 308; Dumas and Piria, *Ann. Chim. Phys.* [3], v. 353; Peligot, *Ann. Chim. Phys.* [3], xii. 562; de la Provostaye, *Ann. Chim. Phys.* [3], iii. 129.

*Normal Potassium Tartrate*, $2C_4H_4O_6K_2 + H_2O$, has been known since the sixteenth century, and was formerly termed *samech Paracelsi*, but afterwards when obtained by neutralizing cream of tartar with salt of tartar (carbonate of potash), it was termed *tartarus tartarisatus*, or *tartarus solubilis*. It was likewise prepared by neutralizing cream of tartar with lime, which was thought to remain in combination with the tartar, until the researches of Marggraf and Roulle proved, in 1770, that the salt obtained by this method also contains no base but potash. It forms monoclinic prisms easily soluble in water, and is used in medicine.

*Acid Potassium Tartrate*, $C_4H_4O_6KH$, is deposited, in the process of fermenting wine, in crystalline crusts containing colouring matter and calcium tartrate, and is known in commerce as argol.

In order to purify the crude tartar it is dissolved in hot water, and the filtered solution allowed to cool. The deposited crystals, which are still coloured, are again dissolved in hot water and recrystallized, some clay or white-of-egg being added in order to absorb the colouring matter. A small quantity of carbonate of potash is also introduced in order to decompose any calcium tartrate which may be present. This latter salt, which frequently occurs in purified cream of tartar, is best removed by heating it with diluted hydrochloric acid and washing with water.

The crude tartar may also be dissolved by carbonate of soda, filtered and precipitated with hydrochloric acid.

Pure cream of tartar forms hard rhombic crystals, having a pleasant sour taste, and being soluble at the ordinary temperature in about 200 parts of cold, and in 15 parts of hot water. It is still less soluble in dilute alcohol, for which reason it is deposited in the fermentation of wine. It is used for the preparation of pure potassium carbonate, in soldering silver, in the processes of tinning and silvering, in dyeing, and for medical purposes, &c.

612 *Normal Sodium Tartrate*, $C_4H_4O_6Na_2 + 2H_2O$, crystallizes in needles or rhombic prisms, easily soluble in water. The *acid salt* crystallizes with one molecule of water, also in the rhombic system. It is much more soluble in water than the corresponding potassium salt.

*Potassium Sodium Tartrate*, $C_4H_4O_6KNa + 4H_2O$, was discovered in 1672 by Seignette, an apothecary in Rochelle, and termed after him Seignette's salt (*sal polychrestum Seignetti*), or

Rochelle salt. The mode of preparation of this salt, which was esteemed as a very valuable medicine, was kept a secret until probably the same chance by which Seignette discovered it made it known to others. This consisted in the use of soda in the place of some of the potash, the differences between the two alkalis not being then recognised. Boulduc obtained the salt in 1731, and in the same year Geoffroy communicated the proofs of manufacture to the Royal Society.[1]

In order to prepare it, a boiling solution of carbonate of soda is neutralized with cream of tartar, and the concentrated solution allowed to cool. The salt crystallizes in large rhombic prisms which dissolve readily in water. It is used as a mild aperient and also for silvering glass (Vol. II., Part I., p. 364).

*Normal Lithium Tartrate* forms an easily soluble uncrystallizable mass. The acid salt, $C_4H_4O_6LiH + H_2O$, deposits in small rhombic crystals which easily dissolve in water.

*The Tartrates of Rubidium and Cæsium.* The acid salts of these metals resemble the potassium salt, but are more easily soluble, especially that of cæsium, the normal salt of which is deliquescent. Upon these properties Bunsen has founded a method for separating these two metals (Vol. II., Part I., p. 172).

613 *Calcium Tartrate,* $C_4H_4O_6Ca + 4H_2O$, is found in the vegetable kingdom, as in grapes and senna leaves. It forms rhombic pyramids or prisms, and is obtained as a crystalline precipitate when a solution of a normal tartrate is mixed with one of calcium chloride. The hydrated salt dissolves in 6,265 parts of water at 15°, and in 352 parts at 100°. The tartrates of the alkali metals dissolve it with formation of double salts. It is soluble in ammoniacal salts and in alkalis. Boiled in alkaline solution it separates out as a jelly.

*Acid Calcium Tartrate,* $(C_4H_5O_6)_2Ca$, occurs according to John in the fruit of the *Rhus typhinum,* and is formed when the freshly prepared normal salt is dissolved in a hot solution of tartaric acid. It forms rhombic crystals dissolving at 15° in 140 parts of water.

*Normal Barium Tartrate,* $C_4H_4O_6Ba + H_2O$, is obtained as an amorphous precipitate which soon becomes crystalline. It is somewhat more soluble in water than the calcium salt, whilst *strontium tartrate,* $C_4H_4O_6Sr + 4H_2O$, is still more soluble, and crystallizes in rhombic tables.

*Lead Tartrate,* $C_4H_4O_6Pb$, is precipitated by tartaric acid from

[1] *Phil. Trans.* abridged vol. ix. 393.

a soluble lead salt as a crystalline powder. It is scarcely soluble in water but dissolves readily in tartaric acid, alkalis, and ammonium salts. When its ammoniacal solution is boiled a crystalline precipitate of $C_2H_2(O_2Pb)(CO_2)_2Pb + H_2O$ is formed, insoluble in water, acetic acid, and ammonium salts, but dissolving in caustic potash.

*Copper Tartrate*, $C_4H_4O_6Cu + 3H_2O$, is formed by precipitating copper sulphate with a normal tartrate. It is a greenish-blue crystalline powder dissolving slightly in cold, but more readily in hot water, and readily in tartaric acid. It dissolves in alkalis with a deep blue colour. Hence copper salts are not precipitated in presence of tartaric acid by caustic potash, &c., each molecule of acid being able to hold in solution one atom of copper,[1] this being due to the formation of the salt, $(CHO)_2Cu(CO_2K)_2$.

*Silver Tartrate*, $C_4H_4O_6Ag_2$, is obtained as a curdy precipitate by precipitating silver nitrate with Rochelle salt. If warm solutions are used it separates out in glistening scales. It soon blackens on exposure to light, and is partially decomposed by boiling water, and completely decomposed in the presence of ammonia with separation of silver.

*The Tartrates of Iron.* Ferrous tartrate, $C_4H_4O_6Fe$, is obtained by continuously boiling together tartaric acid, iron filings, and water. It is a white crystalline powder which is scarcely soluble even in boiling water. Potassium ferrous tartrate is the chief constituent of *Tartarus chalybeatus s. ferratus*, the preparation of which was described by Angelus Sala in the seventeenth century in his *Tartarologia*. This salt, which is used for baths, is prepared by taking 1 part of iron filings and 5 parts of commercial cream of tartar, boiling these with water to a paste, and allowing the whole to stand until a homogeneous black mass is formed, which is then dried.

Ferric tartrate is obtained by dissolving freshly precipitated ferric hydroxide in tartaric acid. The brownish-green solution decomposes on warming with separation of a basic salt, and in the air is partly reduced to ferrous salt. The solution is not precipitated by alkalis. Tartaric acid also prevents the precipitation of salts of other metals of the iron group, as those of chromium, aluminium, copper, zinc, and lead, inasmuch as it forms soluble double salts.[2]

614 *Tartrates of Antimony.* The best known of these is *Potassio-Antimonious Tartrate* or tartar emetic (*tartarus*

[1] Städeler and Krause, *Jahresb.* 1854, 746. [2] Städeler and Krause, *loc. cit.*

*emeticus*, or *tartarus stibiatus*), $2C_4H_4O_6(SbO)K + H_2O$, which was used even in early times as a medicine. The first mention of this salt is found in Mynsicht's *Thesaurus et Armamentarium Medico-chymicum*, in 1631, which contains a receipt for boiling cream of tartar, with *crocus metallorum absinthiacus* (the product obtained by lixiviating the mass obtained by roasting sulphide of antimony with salts of wormwood), filtering the boiling solution and allowing it to crystallize. In his *Furni novi Philosophici*, published in 1648, Glauber describes the preparation of this salt from flowers of spiessglas and cream of tartar, and at a later period a large number of other processes became known for its preparation. Bergman was the first to make known its constituents in his *Dissertatio de tartaro antimoniato*, published in 1773.

In order to prepare tartar emetic 5 parts of purified cream of tartar are boiled with 50 parts of water and 4 parts of antimony trioxide, prepared from the chloride by precipitation with water and treatment of the precipitate with carbonate of soda. The whole is then allowed to stand and crystallize. It forms rhombic prisms with pyramidal faces, and dissolves at the ordinary temperature in about 15 parts of water, and at the boiling point in 2·8 parts. The crystals slowly effloresce on exposure to air, and at 100° quickly fall to a white powder. When the anhydrous salt is heated to 200—220° it loses water, and is converted into the compound $C_4H_2O_6SbK$, a body which dissolves in water with reformation of tartar emetic.[1] Tartar emetic is used in medicine in doses from 0·006 to 0·01 gram, as it acts as a sudorific, but in doses from 0·06—0·2 it acts as an emetic, and in larger doses produces poisonous effects which may become fatal.

The view which is now generally adopted respecting the constitution of tartar emetic is that it is derived from tartaric acid by the replacement of the hydrogen of the carboxyl by an equivalent quantity of the monad radical antimonyl, SbO. Recent investigations by Clarke and Helena Stallo,[2] have, however, led to another explanation. When barium chloride is added to a solution of tartar emetic, a precipitate of the well-known corresponding barium salt is thrown down. If this be decomposed by the requisite quantity of dilute sulphuric acid, a solution is obtained which when neutralised with potash again yields tartar emetic. The acid solution is extremely unstable,

[1] Dumas and Piria, *Ann. Chem. Pharm.* xliv. 85; Schiff, *ib.* cxxv. 129.
[2] *Ber. Deutsch. Chem. Ges.* xiii. 1788.

decomposing quickly with separation of antimonious acid, $Sb(OH)_3$. Hence it is very probable that this is a peculiar acid (of which tartar emetic is the potassium salt), having the following constitution:

$$C_2H_2(OH)_2\begin{matrix}CO.O\\CO.O\end{matrix}>Sb.OH$$

When tartar emetic is dissolved in a solution of tartaric acid, and the whole evaporated to a syrup and slowly cooled, colourless oblique rhombic prisms of the so-called *acid tartar emetic*, $2C_4H_4O_6(SbO)K+C_4H_6O_6+5H_2O$, separate out. This on exposure to the air loses water and changes to a porcelain-like mass, easily decomposed by alcohol into tartar emetic and tartaric acid.

The acid tartrates of the other alkali metals act towards antimony oxide in a similar way to cream of tartar, and yield similar compounds to tartar emetic or salts of *tartryl antimonious acid*. Other similar salts containing metals of other groups are also known. These are only slightly soluble in water, and therefore may be prepared by double decomposition like the above-mentioned barium tartryl antimonite, and the silver salt, $C_4H_4O_7SbAg + H_2O$, which crystallizes from hot water in rhombic tables with diamond-like lustre.[1]

*Antimony Tartrate*, $C_2H_4O_2(CO_2.SbO)_2+H_2O$, is formed by dissolving antimony oxide in tartaric acid, from which solution the salt is precipitated by alcohol as a crystalline powder. At 100° it loses one, and at 190° a second molecule of water, with which it easily recombines. It unites with normal potassium tartrate to form tartar emetic.

*Tartrates of Arsenic.* The oxides of this element comport themselves with acid tartrates like antimony oxide.

*Ammonium Tartryl Arsenite*, $2C_2H_2(OH)_2(CO_2)_2As(ONH_4)+H_2O$, is obtained by boiling acid ammonium tartrate with arsenic trioxide. It forms large, bright, colourless rhombic crystals which easily effloresce.

*Potassium Tartryl Arsenate*, $2C_2H_2(OH)_2(CO_2)_2AsO(OK)+5H_2O$, is obtained by dissolving cream of tartar in arsenic acid. It is precipitated by alcohol as a crystalline powder. It easily decomposes in aqueous solution with separation of cream of tartar.

*Tartrates of Boron.* In 1728 Le Fèvre noticed that cream of tartar is rendered easily soluble by the addition of solution of

[1] Cooke, *Chem. News*, xliv. 233.

borax, and Lasonne, in 1754, found that boracic acid acts in a similar way. Both the preparations thus obtained were termed *tartarus boraxatus*, that with borax being also termed *cremor tartari solubilis*. This compound was much prized by the alchemists, as they believed that by its means the transmutation of the base metals into gold could be effected.

*Potassium Tartryl Borate*, $C_2H_2(OH)_2(CO_2)_2BOK$. This compound is used in medicine (*Tartarus boraxatus Franco-Gallicus*), and is obtained by dissolving 3·5 parts of cream of tartar and 1 part of boric acid in hot water. On evaporating an amorphous transparent mass is obtained which may be rubbed down to a white powder, and is permanent in the air.

The "borax weinstein" of the German pharmacopœia is prepared in a similar way from 2 parts of borax, 5 parts of cream of tartar and twenty parts of water. This is a mixture of potassium sodium tartrate with the foregoing compound, and is distinguished from it inasmuch as it easily absorbs moisture from the air.

615 *The Reactions of Tartaric Acid and its Salts.* When heated these decompose, and a peculiar smell resembling that of burnt sugar but being at the same time somewhat acrid, is evolved. The free acid gives a precipitate of cream of tartar with potassium acetate, the deposition being greatly aided by rubbing the sides of the vessel with a glass rod or by the addition of alcohol. In order to detect tartrates by this test an acid, preferably acetic acid, must be added. The normal tartrates give, with calcium chloride, a precipitate of calcium tartrate, which at the moment of precipitation is amorphous, dissolves pretty easily in an excess of either reagent, and after a short time separates out again in the crystalline form. In dilute solutions the precipitation only takes place after a lapse of some time. Even when the salt does not dissolve again, it soon becomes crystalline. It is soluble in hydrochloric acid, nitric acid, and alkali free from carbonic acid, and from the latter solution it separates out on warming as a gelatinous mass, which slowly dissolves on standing. By these reactions tartaric acid can be distinguished from oxalic, malic, and citric acids, &c. Free tartaric acid is not precipitated by a solution of calcium sulphate, which produces in solutions of normal tartrates a slight precipitate after some time. When a solution of luteo-cobalt chloride is added to one of tartaric acid, and then boiled with caustic soda, the yellow solution becomes green, and then blue-violet. The other vegetable acids

and acetic acid do not give this reaction, all the cobalt being thrown down.[1]

The presence of boric acid interferes with most of the reactions of tartaric acid. In this case, instead of an acetate, potassium fluoride and then acetic acid should be added.[2]

## ETHEREAL SALTS OF TARTARIC ACID.

616 *Acid Ethyl Tartrate,* $C_2H_4O_2\left\{\begin{matrix}CO_2H\\CO_2.C_2H_5.\end{matrix}\right.$ For the preparation of ethyl tartaric acid, equal parts of tartaric acid and absolute alcohol are heated in a retort from 60° to 70°, until two-thirds have come over. The whole is then diluted with water and allowed to evaporate spontaneously.[3] Oblique rhombic very deliquescent prisms then crystallize out, possessing a sweet and pleasant taste, and melting at 90°. Most of its salts crystallize well.

*Normal Ethyl Tartrate,* $C_2H_4O_2(CO_2.C_2H_5)_2$, was first prepared by Demondesir.[4] It is best obtained as follows. A well cooled mixture of equal parts of absolute alcohol and tartaric acid is saturated with hydrochloric acid, the whole being kept cold. After standing for twenty-four hours the clear liquid is poured off, and a current of dry air passed through for some time. The liquid is next warmed to 100°, under diminished pressure, to remove the aqueous hydrochloric acid and the excess of alcohol. An equal volume of alcohol is again added, and the operation repeated, and finally the liquid is distilled under reduced pressure.[5]

Ethyl tartrate is a thick, oily, odourless liquid, having a specific gravity at 14° of 1·2097, and boiling, with slight decomposition, at 280°.

Zinc ethyl, in presence of ether, acts violently on ethyl tartrate, when the following reaction takes place:

$$\begin{matrix}C_2H_5.CO_2.CH.OH\\|\\C_2H_5.CO_2.CH.OH\end{matrix} + Zn(C_2H_5)_2 =$$

$$\begin{matrix}C_2H_5.CO_2.CH.O\\C_2H_5.CO_2.CH.O\end{matrix}\!\!>\!Zn + 2C_2H_6.$$

[1] Braun, *Zeitsch. Anal. Chem.* vii. 349.
[2] Barfoed, *ib.* iii. 292.
[3] Guérin-Varry, *Ann. Chim. Phys.* [2], lxii. 57.
[4] *Compt. Rend.* xxxiii. 327.
[5] Anschütz and Pictet, *Ber. Deutsch. Chem. Ges.* xiii. 1175.

The zinc compound is a snow-white, amorphous, very unstable substance.[1]

When ethyl tartrate is saturated with dry ammonia it forms *tartramide*, $C_2H_4O_2(CO.NH_2)_2$, a body soluble in water and crystallizing in rhombic prisms.[2] If the tartrate be diluted with aqueous ammonia hard crusts of ethyl tartramate are formed. Free *tartramic acid*, $C_2H_4O_2\left\{\begin{matrix}CO.NH_2\\CO.OH\end{matrix}\right.$, is a syrup (Grote).

Hydrogen methyl tartrate closely resembles the ethyl compound. The following are the only normal salts that are known (Anschütz and Pictet):

| | B.P. | Sp. Gr. | at |
|---|---|---|---|
| Methyl tartrate, $C_4H_4O_6(CH_3)_2$ | 280° | 1·3403 | 15° |
| Propyl tartrate, $C_4H_4O_6(C_3H_7)_2$ | 303° | 1·1392 | 17° |

The methyl salt forms hard, white crystals which melt at 48°.

*Dinitroxytartaric Acid*, $C_2H_2(O.NO_2)_2(CO_2H)_2$. This nitric ether, which is ordinarily termed nitro-tartaric acid, is obtained by dissolving powdered tartaric acid in four and a half times the quantity of concentrated nitric acid. On the addition of an equal volume of sulphuric acid it separates out as a gummy mass. This is dried on a porous plate, then dissolved in tepid water, and the solution at once cooled to 0°,[3] when the compound separates out. For purification it is crystallised from ether, and is thus obtained in silky crystals.[4] Its aqueous solution decomposes quickly with formation of oxalic acid and tartronic acid, $CH.OH(CO_2H)_2$, but its solution in absolute alcohol is much more stable, and from this it crystallizes on spontaneous evaporation, sometimes in large prisms. Ammonium sulphide again converts it into tartaric acid.

*Ethyl Dinitroxytartrate*, $C_2H_2(O.NO_2)_2(CO_2.C_2H_5)_2$, is obtained by dissolving ethyl tartrate in a mixture of concentrated sulphuric and nitric acids. The solution is poured into an equal volume of water, when the salt separates out as an oil, which solidifies after some time. Crystallized spontaneously from absolute alcohol, it is deposited in prisms or needles which melt at 45°—46°.[5]

*Ethyl Acetotartrate*, $C_2H_3O(OC_2H_3O)(CO_2C_2H_5)_2$, is obtained

[1] Mulder and van der Meulen, *Ber. Deutsch. Chem. Ges.* xiv. 918.
[2] Grote, *Ann. Chem. Pharm.* cxxx. 202.
[3] Dessaignes, *Compt. Rend.* xxxiv. 731; *Ann. Chem. Pharm.* lxxxii. 362; *Jahresb.* 1857, 306.
[4] Demole, *Ber. Deutsch. Chem. Ges.* x. 1789. [5] Henry, *ib.* iii. 532.

by mixing equal molecules of ethyl tartrate and acetyl chloride. It is a heavy oil with a bitter taste, and decomposes when heated.[1]

*Diacetotartaric Acid*, $C_2H_2(O.C_2H_3O)_2(CO_2H)_2$. The anhydride of this compound is formed by heating tartaric acid with acetyl chloride:[2]

$$\begin{array}{l} CH(OH).CO.OH \\ | \\ CH(OH).CO.OH \end{array} + 4COCl.CH_3 = 4HCl +$$

$$O\begin{array}{l} \diagup CO.CH_3 \\ \diagdown CO.CH_3 \end{array} + \begin{array}{l} CH(O.CH_3.CO)CO\diagdown \\ | \qquad\qquad O. \\ CH(O.CH_3.CO)CO\diagup \end{array}$$

It crystallizes in thin monoclinic needles, melting at 126°—127,° and subliming when further heated. It is easily soluble in alcohol and ether. Its solution in benzol is powerfully dextro-rotatory (Anschütz and Pictet). It is gradually decomposed by water with formation of diacetotartaric acid, a gum-like, very deliquescent mass, which however forms crystalline salts, all of which, even the silver salt, are easily soluble, and for the most part deliquescent. It is remarkable that the solutions of this acid and its salts are lævo-rotatory.

*Ethyl Diacetotartrate*, $C_2H_2(O.C_2H_3O)_2(CO_2.C_2H_5)_2$, is obtained by heating ethyl tartrate with acetyl chloride.[3] It crystallizes from alcohol in transparent strongly-refracting triclinic prisms, and from hot alcohol in long thin needles which have a sharp and bitter taste. It melts at 63°·5, and boils at about 290°, almost without decomposition. Whilst the free acid is decomposed even by boiling with water and very quickly in presence of caustic potash, boiling water only attacks the ethyl salt very slowly, whilst it requires to be boiled with caustic potash for several hours in order to convert it into tartaric acid, acetic acid, and alcohol.

### Anhydrides of Tartaric Acid.

617 It has already been stated (p. 222) that tartaric acid when fused passes into its isomeride, *metatartaric acid*, an amorphous deliquescent mass. The solution of the latter yields tartaric acid again on evaporation. The salts are more readily soluble than the

[1] Perkin, *Journ. Chem. Soc.* N.S. v. 138.
[2] Pilz, *Journ. Prakt. Chem.* lxxxiv. 231; Perkin, *loc. cit.*
[3] Wislicenus, *Ann. Chem. Pharm.* cxxix. 187; Perkin, *loc. cit.*

corresponding tartrates, and yield these on boiling with water.[1] On protracted or strong heating, tartaric acid loses water, and yields compounds whose constitution is probably similar to that of the so-called anhydrides of lactic acid.

*Ditartaric Acid* or *Tartralic Acid*, $C_8H_{10}O_{11}$, is formed by heating tartaric acid for some time to a temperature of 140°—150°. It is an amorphous, exceedingly deliquescent mass, which easily combines with water to form tartaric acid. It is a dibasic acid, and its salts are amorphous, and chiefly resin-like; on heating with water they are converted into acid metatartrates, and these again into the tartrates.[2]

*Tartrelic Acid*, $C_8H_8O_{10}$, is formed when tartaric acid is heated for some time to 180° (Fremy), or when it is strongly heated until it yields a sponge-like blackened mass (Laurent and Gerhardt). It forms deliquescent crystals, and on fusing with tartaric acid it is converted into tartralic acid (Schiff). Boiling with water converts it into tartralic and tartaric acids. Alcohol precipitates the salts of the alkali metals from their solutions as oils, and they dissolve in water with formation of ditartrates. The salts of the alkaline earth and other metals are obtained by precipitating the free acid with the corresponding acetates, and pass in contact with water into the metatartrates.

*Tartaric Anhydride.* This substance is isomeric with the foregoing body, and is obtained either by heating tartaric acid to 180° until an infusible residue is formed (Fremy), or by heating freshly-prepared tartrelic acid for a short time to 150° (Laurent and Gerhardt). It is a white or yellowish powder, insoluble in alcohol or ether. It dissolves slowly in cold, and quickly in boiling water, when it is first converted into tartrelic acid, and by further addition of water passes into tartralic acid.

## RACEMIC ACID AND LÆVOTARTARIC ACID.

618 It was formerly believed that racemic acid, often obtained as a by-product in the manufacture of tartaric acid, was contained in the grape-juice, and it is quite possible that this is sometimes the case. There is, however, no doubt that the greater portion

[1] Erdmann, *Ann. Chem. Pharm.* xxi. 9; Laurent and Gerhardt, *ib.* lxx. 348.
[2] Fremy, *Ann. Chim. Phys.* [2] lxviii. 353; Laurent and Gerhardt, *loc. cit.*; Schiff, *Ann. Chem. Pharm.* cxxv. 129.

is formed during the manufacture of the wine. According to Jungfleisch the change of tartaric acid into racemic acid takes place very readily in presence of alumina.[1] Dessaignes has shown that several per cents of racemic acid are formed when tartaric acid is mixed with dilute hydrochloric acid[2] or even when it is boiled several days with water.[3] In Kestner's manufactory, in which racemic acid was first observed, no further production of this substance has been noticed since the solutions have been evaporated in a vacuum at 50°. On the other hand, in a Viennese manufactory, where superheated steam is employed, the mother-liquors contain a large quantity of mesotartaric acid and some racemic acid, and in an English manufactory in which the evaporation takes place at the ordinary pressure, large quantities of this latter acid are still formed.[4]

Pasteur was the first to show that tartaric acid can be converted into racemic acid. He found that when cinchonine tartrate is heated for some time to 170°, racemic acid is formed, together with inactive tartaric acid, and also that the lævorotatory salt of this alkaloid and ethyl tartrate undergo this change.[5] Racemic acid is best obtained by heating tartaric acid with water in the proportion of 30 grams of the first to from 3 to 4 cbc. of the latter, for 30 hours, to a temperature of 175°, when the change is almost complete.[6] A transformation of calcium tartrate into racemate is found to occur in dye-vats in which tartaric acid has been used to liberate chlorine from bleaching powder.[7] Another singular formation of racemic acid is that by the oxidation of fumaric acid with potassium permanganate,[8] when a direct addition of hydroxyl takes place.

Racemic acid crystallizes in triclinic prisms containing a molecule of water which is driven off at 100°. It is less soluble in water than tartaric acid, 100 parts of water at 20° dissolving only 22·66 parts. It melts at 202°, and yields on further heating, the same products as tartaric acid. It is more easily reduced to succinic acid by means of hydriodic acid than is tartaric acid (Lautemann), and as intermediate product the modification of malic acid corresponding to racemic acid is formed (p. 202).

[1] *Bull. Soc. Chim.* [2], xxi. 146 ; xxx. 191.
[2] *Compt. Rend.* xlii. 494 and 524.
[3] *Bull. Soc. Chim.* v. 355.
[4] *Ber. Entw. Chem. Ind.* ii. 423.
[5] *Compt. Rend.* xxxvii. 162.
[6] Jungfleisch, *Bull. Soc. Chim.* [2], xviii. 203.
[7] Lidow, *Ber. Deutsch. Chem. Ges.* xiv. 2689.
[8] Kekulé and Anschütz, *ib.* xiii. 2150.

The racemates in general closely resemble the tartrates, though they frequently contain different quantities of water of crystallization. Like the acid, they are optically inactive and do not like the tartrates exhibit hemihedral faces.

*Normal Potassium Racemate,* $C_4H_4O_6K_2+2H_2O$, forms monoclinic crystals, easily soluble in water.

*Acid Potassium Racemate,* $C_4H_4O_6KH$, crystallizes in rhombic tables, dissolving more readily in water than cream of tartar, and forming with antimony oxide a compound similar to tartar emetic.

*Calcium Racemate,* $C_4H_4O_6Ca+4H_2O$, is the most characteristic salt of racemic acid. It is a precipitate consisting of small needles, more difficultly soluble than the tartrate, and precipitated, even from a solution of the free acid, by calcium sulphate. It does not dissolve in acetic acid, but is soluble in hydrochloric acid, and on addition of ammonia it is at once thrown down, whilst in the case of the tartrate, precipitation takes place only after standing some hours.

The *ethereal salts of racemic acid* closely resemble those of tartaric acid, and are optically inactive :—

| | M.P. | B.P. |
|---|---|---|
| [1] Methyl racemate, $C_2H_2(OH)_2(CO_2.CH_3)_2$ | 85° | 282° |
| [2] Ethyl diacetoracemate, $C_2H_2(C_2H_3O_2)_2(CO_2.C_2H_5)_2$ | 50°·5 | 298° |
| [3] Diacetoracemic anhydride, $C_2H_2(C_2H_3O_2)_2C_2O_3$ | 123° | — |

619 *Pasteur's Researches.* The discovery that racemic acid can be decomposed into two active acids was made by Pasteur. He showed that the salts of tartaric acid usually exhibit hemihedral faces, whilst those of racemic are holohedral. On crystallizing a solution of ammonium sodium racemate, a salt which Mitscherlich believed to be isomorphous with the corresponding tartrate, Pasteur found that although all the crystals were hemihedral, the hemihedral faces were situated on some crystals to the right, and on others to the left hand of the observer, so that the one formed, as it were, the reflected image of the other, as in Figs. 102—107, these faces being distinguished by the symbols $+\frac{P}{2}$ and $-\frac{P}{2}$. Pasteur separated these two sets of crystals mechanically, and purified them by recrystallization, when he found that they do not undergo alteration in form, and that

[1] Anschütz and Pictet, *Ber. Deutsch. Chem. Ges.* xiii. 1178.
[2] Perkin, *Journ. Chem. Soc.* N.S. v. 138.
[3] Perkin ; Anschütz and Pictet.

those which exhibited dextro-hemihedry possess dextro-rotatory power, whilst the others are lævo-rotatory. He then converted these into the lead salts, and on decomposing with sulphuretted hydrogen, obtained both the free acids, one of which proved to be identical with common tartaric acid, whilst the other was distinguished from it, inasmuch as it turns the plane of polarization as powerfully to the left as common tartaric acid does to the

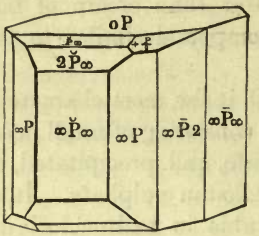



Fig. 102.

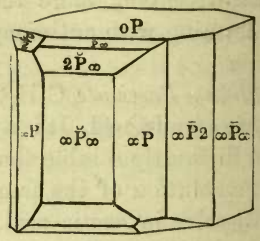



Fig. 103.

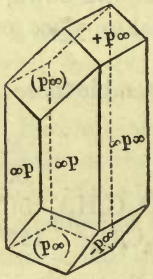



Fig. 104.

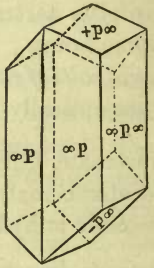



Fig. 105.

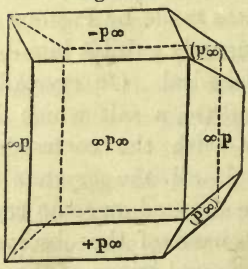



Fig. 106.

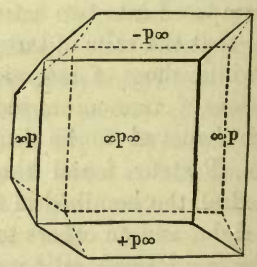



Fig. 107.

right, and for this reason Pasteur termed it lævo-tartaric acid, or anti-tartaric acid. The acids moreover are positively and negatively hemihedral, as is shown by the following figures in which the hemihedral faces are marked. Both the acids are pyro-electrical, but each in an opposite sense, inasmuch as positive electricity is developed on the side of the crystal on which hemihedry occurs.

If equal quantities of the concentrated solutions of the two acids be mixed, an evolution of heat takes place, and crystals of racemic acid separate out. Their salts behave in the same way, and otherwise exhibit the same properties. They contain the same quantity of water of crystallization, and possess the same degree of solubility.

On the other hand, they show an altogether different reaction in their combinations with optically active compounds. Thus hydrogen ammonium tartrate forms, with the hydrogen ammonium salt of common malic acid, a crystallizable double salt, whilst the salt of lævo-tartaric acid does not do so. Dextro-tartaric acid combines also with asparagin to form a crystalline compound, but this compound cannot be obtained with the lævo-tartaric acid. Each of the optically active alkaloids, cinchonicine, chinicine, strychnine, and brucine, yields a normal and an acid salt with the two tartaric acids. The eight salts of the one modification are distinguished from the corresponding ones of the other modification by crystalline form, quantity of water of crystallization, and solubility, and these varying relations serve as another means for resolving racemic acid into its constituent acids. If a solution of cinchonicine in racemic acid be concentrated, at first only the lævo-tartaric acid salt separates out, whilst when chinicine is employed the dextro-tartaric salt first makes its appearance.

Pasteur has further shown that when a few spores of *penicillium glaucum* are added to a solution of racemic acid containing traces of phosphates, dextro-tartaric acid first disappears, so that if the fermentation be stopped after some time, only the lævo-acid remains.[1]

Lastly, Gernez has found that a saturated solution of the ammonium sodium salt, does not crystallize when a crystal of the opposite modification is brought into it. Hence, if such a solution be prepared from racemic acid, it is easy to obtain either one or the other modification in this way at will.[2]

In order to explain the optical isomerism of the two tartaric acids, we may assume that in their molecules the atoms occupy different positions in space. This can be best illustrated by means of a model consisting of a tetrahedron in whose centre an asymmetrical carbon atom is situated, the four combining units being placed in connection with the corners. On these the several groups $H,OH,CO_2H$ and $CH(OH)CO_2H$ are

[1] *Comptes Rendus*, li. 153. [2] *Ib.* lxiii. 843.

joined. They may be distinguished by painting the four points of different colours. A second tetrahedron is then prepared which is, as it were, the reflected image of the first. One of the two models represents the dextro- and the other the lævo-tartaric acid, and in whatever position they may be placed they are always seen to be right- and left-handed.[1]

## INACTIVE OR MESO-TARTARIC ACID.

620 This acid was obtained by Pasteur, together with racemic acid, by heating cinchonine tartrate to 170°. In this decomposition it is probable that the racemate is first formed, as this, when heated by itself, partially decomposes into the inactive compound. By the oxidation of sorbin, $C_6H_{12}O_6$, Dessaignes obtained, in addition to tartaric and racemic acids, an inactive isomeric compound to which he gave the name of mesotartaric acid, and Pasteur afterwards showed that this was identical with his acid. It has already been stated that this acid usually occurs together with racemic acid (p. 234).

Mesotartaric acid is best obtained by heating thirty parts of tartaric acid and four parts of water for two hours to 165°. On crystallizing, the racemic acid which has been formed deposits first. The residue is converted into the acid potassium salt, when cream of tartar separates out, whilst the more soluble salt of the inactive acid remains in solution.[2] By this reaction the other modifications are also almost entirely converted into mesotartaric acid, whilst at 175° they, as well as the last named acid, are almost entirely transformed into racemic acid. In this way Jungfleisch has succeeded in preparing the four modifications synthetically from ethylene.

It is an interesting fact that the inactive acid is also formed by oxidation of maleic acid by potassium permanganate, whilst fumaric acid is oxidized to racemic acid. From this, it would appear that the cause of the isomerism of maleic acid is the same as that of mesotartaric acid and racemic acid.[3]

Mesotartaric acid crystallizes in rectangular tables, with one molecule of water, which it losses at 100°. When the anhydrous acid is dissolved in a small quantity of water and allowed to

[1] Van't Hoff, *Lagerung der Atome, &c.*
[2] Jungfleisch, *Bull. Soc. Chim.* [2], xix. 101.
[3] Kekulé and Anschutz, *Ber. Deutsch. Chem. Ges.* xiv. 713; compare Tanatar, *ib.* xiii. 1383.

crystallize quickly, it is obtained in anhydrous prisms closely resembling those of tartaric acid. One hundred parts of water at 15° dissolve 125 parts of the crystallized acid. The crystals melt at 140°, and when submitted to dry distillation yield pyro-racemic acid; if the distillation be stopped when a third has passed over, racemic acid may be prepared from the residue (Dessaignes).

The normal and acid mesotartrates are easily soluble in water, but do not crystallize.

*Calcium Mesotartrate*, $C_4H_4O_6Ca+3H_2O$, is a very characteristic salt, and is formed when the acid is precipitated by calcium acetate. The flocculent precipitate soon changes to glistening crystals, which are best obtained when the salt is dissolved in hydrochloric acid and so far diluted that ammonia does not produce a precipitate. After standing from 12 to 16 hours, it is desposited in bright, glistening, cube-like crystals. It dissolves in about 600 parts of boiling water, and separates very gradually on cooling in small compact crystals and small four-sided prisms. It is insoluble in acetic acid, and is not formed by the addition of sulphate of lime solution to a solution of mesotartaric acid.

The inactive acid obtained from glyoxal (p. 220) is different from mesotartaric acid, and it may therefore be distinguished as *glycotartaric acid*.[1] Like racemic acid, which it was first believed to be, it crystallizes in triclinic prisms containing one molecule of water, and these do not effloresce on exposure. The anhydrous acid melts at 198°. Its salts resemble very closely those of racemic acid, but the sodium ammonium glycotartrate is deposited in large monoclinic crystals which do not exhibit hemihedral faces. It is remarkable that racemic acid can, under certain circumstances, yield a salt having the same properties as the preceding compound, the mother-liquors afterwards depositing rhombic crystals of the two optically active salts.[2]

A third inactive tartaric acid has been obtained by Przibytek by the oxidation of erythrite, $C_4H_6(OH)_4$. The acid potassium salt of this variety is anhydrous, easily soluble in water, and crystallizes in small needles. The calcium salt contains 8 molecules of water, is soluble in acetic acid, and crystallizes from this solution in laminæ. When the acid is heated with water to 175°, it is converted into racemic acid.

[1] Staedel and Gail, *Ber. Deutsch. Chem. Ges.* xi. 1752.
[2] *Journ. Russ. Chem. Ges.* xii. 209.

# THE PENTYLENE COMPOUNDS.

621 By heating amyl alcohol with concentrated solution of zinc chloride, Balard, in 1844, obtained the corresponding olefine termed *amylene*, $C_5H_{10}$, and together with this the polymeride *diamylene*, $C_{10}H_{20}$, and *tetramylene*, $C_{20}H_{40}$. Moreover, he showed that when the vapour of amyl chloride is passed over heated potash-lime, amylene is also formed. It possesses a faint garlic-like smell, boils at 39°, and has a vapour density of 2·68.[1]

Bauer, who then occupied himself with this subject, gives the following receipt for its preparation. One part of amyl alcohol is poured on to 1½ parts of fused and roughly powdered zinc chloride, allowed to stand for some days, and afterwards distilled. The action begins at 70°—80°, and the operation is stopped at 130°—140°, when frothing begins. By fractionating the distillate and rectifying over sodium, the amylene is obtained together with amyl hydride, $C_5H_{12}$. Amylene thus prepared boils at 33°—34° and at 0° has a specific gravity of 0·663. In the higher boiling portions *triamylene*, $C_{15}H_{30}$, occurs, together with the other products obtained by Balard.[2]

As Wurtz has shown, the action of zinc chloride on amyl alcohol is not so simple a one as had formerly been supposed. He found that the product boiling at 160°, is a mixture of the olefines $C_5H_{10}$ to $C_{10}H_{20}$, and of the corresponding paraffins.[3]

Recent investigations have proved that the amylene thus obtained, and now to be bought as "commercial amylene," is not a definite compound, but a mixture of several isomeric bodies, their formation depending not only on the fact that amyl alcohol itself is a mixture, but also that zinc chloride effects a molecular decomposition in this case, as it does in the case of butylene.

[1] *Ann. Chim. Phys.* [3], xii. 320.
[2] *Krit. Zeitsch.* iv. 654; see also Linnemann, *Ann. Chem. Pharm.* cxxxiv. 350.
[3] *Comptes Rendus*, lvi. 1164 and 1246; lvii. 392; *Ann. Chem. Pharm.* cxxviii. 225 and 316.

Amylene is also found in the distillation products of Boghead cannel, in the lime soap of train oil, and in certain petroleums, &c.

622 *Propyl Ethylene*, $CH_3.CH_2.CH_2.CH=CH_2$, was obtained synthetically by Wurtz by the action of zinc-ethyl on allyl iodide. He could not, however, obtain it in a pure state. owing to the formation of other hydrocarbons.[1] *Pentylene dibromide*, $C_5H_{10}Br_2$, obtained from this, boils at 177°—183°. Normal pentylene is also formed together with ethereal salts of pentyl-acetic acid when the monochloride, obtained from normal petane, is heated with potassium acetate and glacial acetic acid to 190°—200°.[2] Moreover, it is a constituent of commercial amylene. If this liquid be shaken up with a mixture of one volume of water and two volumes of sulphuric acid, the isomeric olefines dissolve and a mixture of the normal pentylene and pentanes remains behind.[3] By oxidizing this with an alcoholic solution of potassium permanganate, formic, oxalic, normal butyric, and succinic acids are formed, and from this fact the constitution of these hydrocarbons is ascertained.[4] Owing to the fact that Balard purified his amylene by treatment with sulphuric acid, it likewise chiefly consisted of propyl-ethylene. It is a mobile liquid, boiling between 39° and 40°, and combining with hydriodic acid to form methyl-propyl-carbyl iodide.

*Isopropyl-ethylene*, $(CH_3)_2CH.CH=CH_2$, occurs, according to Eltekow, in commercial amylene.[5] It is formed together with $\beta$-ethyl-methyl-ethylene, when amyl iodide is heated with alcoholic potash. If this mixture be saturated at — 20° with hydriodic acid, the latter olefine is converted into dimethyl-ethyl-carbyl iodide, isopropyl-ethylene remaining unchanged. When the above mixture is shaken up with sulphuric acid and water, the $\beta$-ethyl-methyl-ethylene is alone dissolved. Isopropyl-ethylene boils at 21°·1 to 21°·3, and combines at the ordinary temperature with hydriodic acid to form methyl isopropyl carbyl iodide (Wischnegradsky). With bromine it forms a dibromide boiling with decomposition at 190°, from which *isopropyl-ethylene glycol*, $(CH_3)_2CH.CH(OH).CH_2(OH)$, is obtained. This latter body boils at 206°, and is a thick odourless liquid, soluble in

[1] *Compt. Rend.* liv. 387 ; lvi. 354 ; lxvi. 1179 ; *Ann. Chem. Pharm.* cxxiii. 202 ; cxxvii. 55 ; cxclviii. 131.
[2] Schorlemmer, *Phil. Trans.* 1872, p. 111.
[3] Wischnegradsky, *Ann. Chem. Pharm.* cxc. 346.
[4] O. and F. Zeidler, *ib.* cxcvii. 253.
[5] *Ber. Deutsch. Chem. Ges.* x. 1904.

water, and yielding on oxidation *oxyvaleric acid*, and *isobutyric acid*.[1]

623 *a-Ethyl-methyl-ethylene*, $CH_3.CH_2.CH{=}CH.CH_3$, is obtained by heating the two secondary pentyl iodides with alcoholic potash.[2] The pentylene obtained by Beilstein and Rieth by the action of zinc-ethyl on chloroform appears to be identical with this substance :[3]

$$3Zn(CH_2.CH_3)_2 + 2CH.Cl_3 = 2CH_3.CH_2.CH{=}CH.CH_3 + 2C_2H_6 + 3ZnCl_2.$$

It boils at 36°, and combines with hydriodic acid forming methyl-propyl-carbyl iodide.

*a-Ethyl-methyl-ethylene Bromide*, $C_2H_5.CHBr.CHBr.CH_3$, boils with slight decomposition at 178°, and at 0° has a specific gravity of 1·7087.

*a-Ethyl-methyl-ethylene Glycol*, $C_2H_5.CH(OH).CH(OH).CH_3$ is a syrupy liquid, soluble in water, boiling at 187°·5, and at 0° having a specific gravity of 0·9945. When oxidized with dilute nitric acid it yields *a-oxybutyric acid*, together with carbon dioxide and a small quantity of glycolic acid.

*β-Ethyl-methyl-ethylene*, $C_2H_5(CH_3)C{=}CH_2$. This is a constituent of commercial amylene (Wischnegradsky), and is formed together with isopropyl-ethylene by heating amyl iodide with alcoholic potash, and is also prepared in a similar way from active amyl iodide.[4] A pentylene, probably identical with this, is found in the distillation products of the Alsatian petroleum at Pechelbronn.[5] It boils at 31°—32°, and at 0° has a specific gravity of 0·670. It is optically inactive, dissolves readily in dilute sulphuric acid, and combines with the haloid acids with formation of ethereal salts of dimethyl-ethyl-carbyl.

624 *Trimethyl-ethylene*, $(CH_3)_2C{=}CH.CH_3$, is also found in commercial amylene, and is formed by the action of alcoholic potash on the iodides of dimethyl-ethyl-carbyl, and isopropyl-methyl-carbyl.[7] It is formed also when amyl ethyl ether is heated with phosphorus pentoxide.[8]

[1] Flawitzky, *Ann. Chem. Pharm.* clxxix. 351 ; *Ber. Deutsch. Chem. Ges.* x. 230.
[2] Wagner and Saytzeff, *Ann. Chem. Pharm.* clxxv. 373 ; clxxix. 302.
[3] *Ib.* cxxiv. 245.
[4] Le Bel, *Bull. Soc. Chim.* [2], xxv. 543.
[5] Le Bel, *ib.* [2], xvii. 3 ; xviii. 166.
[6] Jermolajew, *Zeitsch. Chem.* 1871, 275.
[7] Wischnegradsky, *Ann. Chem. Pharm.* cxc. 365.
[8] Flawitzky, *ib.* clxix. 206.

It is a liquid boiling at 36°—38°, and having at 0° a specific gravity of 0·6783. It is easily converted into polyamylenes by zinc chloride or by dilute sulphuric acid, as well as by boron fluoride.[1] It dissolves when shaken with a mixture of two parts of sulphuric acid and one of water, and when this solution is neutralized with carbonate of soda and distilled, dimethyl-ethyl-carbinol is obtained, which combines with the haloid acids to form the ethereal salts of this alcohol.

The derivatives of the pure hydrocarbon have not been much investigated, but these probably form a large portion of the compounds obtained from commercial amylene.

625 *Amylene Glycol*, $C_5H_{10}(OH)_2$, was obtained by Wurtz[2] from amylene bromide in the same way as common glycol is obtained from ethylene bromide. It is a colourless syrupy liquid, soluble in water, and having an aromatic bitter taste; it boils at 177,° and at 0° has a specific gravity of 0·987. It may be solidified in a mixture of ether and solid carbon dioxide to a hard transparent mass. Pure trimethyl-ethylene yields a glycol which boils at the same temperature.[3] Dilute nitric acid oxidizes it to *oxyisobutyric acid.*

*Amylene Chlorhydrate*, $C_5H_{10}Cl(OH)$, was obtained by Carius by acting on amylene with dilute hypochlorous acid. It is a liquid boiling at 155°, smelling of valeric acid, and is tolerably soluble in water. Caustic potash converts it into *amylene oxide*, $C_5H_{10}O$, a pleasantly smelling liquid having a bitter taste, boiling at 95°, and having a specific gravity at 0° of 0·8244.[4]

*Amylene Chloride*, $C_5H_{10}Cl_2$, is formed when a mixture of amylene and phosphorus pentachloride is allowed to stand for twelve hours. On addition of water it separates out as an oily layer.[5] It is also formed, together with substitution-products, when chlorine is passed into amylene cooled to —15°, and then heated gradually to the boiling point.[6] It is a liquid boiling at 145°, and having at 0° a specific gravity of 1·222.

*Amylene Bromide*, $C_5H_{10}Br_2$, is an oily liquid boiling with decomposition at 170°—180°.

*Amylene Nitrite*, $C_5H_{10}(NO_2)_2$, was first obtained by Guthrie by passing amylene vapour, mixed with air, through fuming

[1] Landolph, *Ber. Deutsch. Chem. Ges.* xii. 1584.
[2] *Ann. Chim. Phys.* [3], lv. 458.
[3] Flawitzky, *Ber. Deutsch. Chem. Ges.* ix. 1600.
[4] Bauer, *Ann. Chem. Pharm.* cxv. 90; Carius, *ib.* cxxvi. 199; cxxix. 167.
[5] Guthrie, *Quart. Journ. Chem. Soc.* xiv. 127.
[6] Bauer, *Zeitsch. Chem.* 1866, 380 and 667.

nitric acid,[1] and afterwards by passing nitrogen trioxide through amylene placed in a freezing mixture.[2] It crystallizes from boiling ether in long transparent prisms or rectangular tables, which decompose at 95°. When treated with tin and hydrochloric acid, the nitrogen is evolved as ammonia.

*Amylene Nitrosochloride*, $C_5H_{10}(NO)Cl$, is formed by the direct union of nitrosyl chloride with amylene. It deposits in splendid crystals, and is converted by nascent hydrogen into an amylamine.[3]

Amylene forms, with the chlorides of sulphur, compounds which correspond to the ethylene compounds.[4]

*Nitro-amylene*, or *Nitro-trimethyl-ethylene*, $C_5H_9NO_2$, is obtained by the action of nitric acid on dimethyl-ethyl carbinol. It is a slightly coloured peculiarly smelling liquid, boiling at 166°—170°, and dissolving slowly in potash. The solution gives the pseudo-nitrol reaction (Part I. p. 566) with potassium nitrite and sulphuric acid. When heated with water to 100° under pressure, it splits up into nitro-ethane and acetone:[5]

$$\begin{array}{l} CH_3 \\ | \\ C{=}C(NO_2).CH_3 \\ | \\ CH_3 \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + CH_2(NO_2).CH_3.$$

## THE OXYACIDS, $C_5H_{10}O_3$, AND THE KETONIC ACIDS, $C_5H_8O_3$.

626 *a-Oxyvaleric Acid*, $(CH_3)_2CH.CH(OH)CO_2H$. When valeric acid is heated with bromine under pressure *a-bromvaleric acid* $(CH_3)_2CH.CHBr.CO_2H$, is formed. This is an oily liquid which decomposes on heating.[6] If this body be boiled with water and oxide of silver or with caustic potash,[7] the corresponding oxyvaleric acid is obtained, a substance which can also be prepared synthetically from isobutyraldehyde. This compound combines with anhydrous hydrocyanic acid to form the nitril

[1] *Quart. Journ. Chem. Soc.* xiii. 35. [2] *Ib.* xiii. 139.
[3] Tönnies, *Ber. Deutsch. Chem. Ges.* xii. 169.
[4] Guthrie, *Quart. Journ. Chem. Soc.* xii. 109; xiii. 35.
[5] Hartinger, *Monatsh. Chem.* ii. 286.
[6] Fittig and Clark, *Ann. Chem. Pharm.* cxxxix. 199; Ley and Popow, *ib.* clxxiv. 63.
[7] Schmidt and Sachtleben, *ib.* cxciii. 106.

$(CH_3)_2CH.CH(OH)CN$, a liquid which commences to boil at 136°, and then decomposes into the compounds from which it is derived. When boiled in connection with an inverted condenser with three times its volume of concentrated hydrochloric acid oxyvaleric acid is obtained, which then may be removed by shaking with ether.[1] It is easily soluble in water, alcohol, and ether, and crystallizes in rectangular tables or long prisms which melt at 86°, and begin to volatilize at 100°. Its chemical relations are closely analogous to those of lactic acid. On heating with sulphuric acid it is converted into formic acid and isobutyraldehyde. The latter compound is also formed, together with isobutyric acid and carbon dioxide, when it is oxidized with aqueous chromic acid.

The crystallized anhydrous zinc salt is difficultly soluble in cold, and not much more soluble in hot water. The silver salt dissolves tolerably easily in hot water, and forms feather-like crystals. By the action of ethyl iodide it yields the ethyl salt, which is also formed when ethyl oxalate is treated with zinc and secondary propyl iodide.[2] It is a not unpleasantly smelling liquid, boiling at 175°.

*α-Valerolactide*, $C_{10}H_{16}O_4$, is formed when the acid is heated in closed tubes to 200°. It crystallizes from dilute alcohol in thin needles insoluble in water, melting at 136°, and subliming at a higher temperature. It is scarcely attacked by dilute alkalis.

*α-Oxyvaleramide*, $(CH_3)_2CH.CH(OH).CO.NH_2$, is formed by the action of cold fuming hydrochloric acid on the nitril. It crystallizes in large tablets which are tolerably soluble in water, less so in ether, and which melt at 104° (Lipp).

*α-Amidovaleric Acid*, $(CH_3)_2CH.CH(NH_2).CO_2H$. A compound of this composition was found by Gorup-Besanez in the pancreas of the ox, and he termed it *butalanine*.[3] This compound closely resembles the acid obtained by heating bromvaleric acid with ammonia. The latter compound is easily soluble in water, scarcely soluble in cold alcohol, and crystallizes in laminæ consisting of microscopic prisms which, on heating, sublime without melting (Fittig and Clark ; Schmidt and Sachtleben). Further investigations have shown that butalanine is different from *α*-amidovaleric acid, and it differs also in its properties from *α*-amidopentoic acid, $CH_3.CH_2.CH_2.CH(NH_2)CO_2H$, which

[1] Lipp, *Ann. Chem. Pharm.* ccv. 23.
[2] Markownikow, *Zeitsch. Chem.* 1870, 517.
[3] *Ann. Chem. Pharm.* xcviii. 15.

latter is obtained from brompentoic acid,[1] and from normal butyroaldehyde ammonia and hydrocyanic acid.[2] Butalanine is probably ethyl methyl amidoacetic acid, $C_2H_5(CH_3)CH(NH_2).CO_2H$.

627 *β-Oxyvaleric Acid*, $(CH_3)_2C(OH).CH_2.CO_2H$, was first prepared by M. and A. Saytzeff by oxidizing dimethyl allyl carbinol, $(CH_3)_2C(OH).CH_2.CH{=}CH_2$.[3] It is also formed by the action of potassium permanganate on valeric acid.[4] It forms a syrup easily soluble in water, alcohol, and ether. It is not volatilized in a current of steam, and on heating with a chromic acid solution it yields acetic acid, acetone, and carbon dioxide, and when heated it decomposes into water and dimethyl-acrylic acid, $(CH_3)_2C{=}CH.CO_2H$.

The anhydrous zinc salt crystallizes in prisms which are easily soluble in water. The silver salt, which does not undergo change on exposure to light, forms monoclinic prisms and is very difficultly soluble in cold water, though rather more soluble in boiling water. It forms with ethyl iodide an ethereal salt boiling at about 180°.[5]

*β-Amidovaleric* or *Amido-dimethyl-propionic Acid*, $(CH_3)_2C(NH_2)CH_2.CO_2H + H_2O$, is formed together with amido-isobutyric acid by the oxidation of diacetonamine (Part I. p. 574). It is easily soluble in water and separates out from a mixture of ether and alcohol in glistening crystals melting at 217°, but beginning to sublime at 180°.

*Imido-dimethylacetic-dimethylpropionic Acid*, $NH\langle^{C(CH_3)_2CH_2.CO_2H}_{C(CH_3)_2CO_2H}$, is formed, together with a small quantity of the foregoing compound, by the oxidation of triacetonamine (Part I. p. 574). It forms a crystalline powder possessing an acid taste, difficultly soluble in cold, but readily soluble in hot water, and very slightly soluble in alcohol.

*α-Methyloxybutyric* or *Metho-ethoxalic Acid*, $(C_2H_5).C(CH_3)OH.CO_2H$. The ethyl salt of this acid is formed when ethyl oxalate is heated with granulated zinc, methyl iodide and ethyl iodide, to 35°—40°.[6] It is also formed by the oxidation of methyl-ethyl-acetic acid with potassium permanganate,[7] and likewise

[1] Juslin, *Bull. Soc. Chim.* xxxvii. 3. [2] Lipp, *Lieb. Ann.* ccxi. 354.
[3] *Ann. Chem. Pharm.* clxxxv. 163; Schirokow, *Journ. Russ. Chem. Ges.* xi. 410.
[4] Miller, *Ann. Chem. Pharm.* cc. 273.
[5] Semljanitzin and Saytzeff, *Ann. Chem. Pharm.* cxcvii. 72.
[6] Frankland and Duppa, *Proc. Roy. Soc.* xiv. 17.
[7] Miller, *Ann. Chem. Pharm.* cc. 282.

when methyl-ethyl ketone is combined with hydrocyanic acid and the product decomposed by hydrochloric acid, and lastly when ethyl-methyl-acetic acid is converted into the monobrominated acid by heating with bromine and this afterwards decomposed with carbonate of soda.[1]

It is easily soluble in water, alcohol and ether, melts at 68° and sublimes in needles at 90°. Aqueous chromic acid oxidizes it to methyl-ethyl ketone and carbon dioxide,[2] and when heated for 200 hours with dilute sulphuric acid to 115°—130° it decomposes into water and methyl-crotonic acid, $CH_3CH{=}C(CH_3).CO_2H$. The anhydrous zinc salt is a crystalline precipitate difficultly soluble in boiling water and insoluble in alcohol. The ethyl salt is a liquid possessing a powerful ethereal smell, boiling at 165°·5, and having a specific gravity at 13° of 0·9768.

628 *β-Methyloxybutyric Acid*, $CH_3.CH(OH).CH(CH_3).CO_2H$, is formed when an alcoholic solution of ethyl methyl-acetacetate is treated with sodium amalgam. In order to prevent the decomposition of the ether into carbon dioxide and methyl-ethyl ketone, the liquid is well-cooled and from time to time acidified with dilute sulphuric acid.[3] The acid forms a syrup which on standing over sulphuric acid becomes thicker and is converted into the anhydride $C_{10}H_{18}O_5$. The acid decomposes on distillation, into water and methyl-crotonic acid.

*Methyl Acetoacetic Acid*, or *α-Acetylpropionic Acid*, $CH_3.CO.CH(CH_3).CO_2H$. The ethereal salts of this acid are prepared according to a process already described (p. 172), and are similar to the acetoacetates. The methyl salt boils at 177°·4 and yields with ferric chloride a violet-red coloration[4] and the ethyl salt boils at 186°·8, has a specific gravity at 6° of 1·009, and gives a deep blue colour with ferric chloride.[5]

It has been stated under acetoacetic acid (p. 172) that only its salts had been prepared. Since this was written the free acid, and also certain of its homologues, have been isolated. The ethereal salt is slowly saponified by cold dilute potash solution; this then, after standing twenty-four hours, acidified with sulphuric acid, is shaken up with ether, and the ethereal solution cautiously evaporated, when a mixture remains of the free acid and

[1] Böcking, *Ann. Chem. Pharm.* cciv. 18.
[2] Chapman and Smith, *Journ. Chem. Soc.* N.S. v. 296.
[3] Rohrbeck, *Ann. Chem. Pharm.* clxxxviii. 229; Miller, *ib.* cc. 269.
[4] Brandes, *Zeitsch. Chem.* 1866, 458. [5] Geuther, *Jahresb.* 1865, 303.

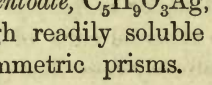
the unattacked salt. This latter is removed by rubbing up the residue with water and barium carbonate, and isolating the acid from the resulting barium salt by the process just described.

Acetoacetic acid is a thick, strongly acid liquid, which decomposes violently, even below 100°, into carbon dioxide and acetone; and methyl-acetoacetic acid comports itself in an exactly corresponding manner.[1]

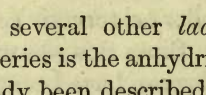
*α-Amidopentoic Acid*, $CH_3.CH_2.CH_2.CH(NH_2.)CO_2H$, is obtained by the action of ammonia on *α*-brompentoic acid, and crystallizes from water in long prismatic needles.[2]

629 *γ-Oxypentoic Acid*, $CH_3.CH(OH).CH_2.CH_2.CO_2H$, is not known in the free state, but its anhydride termed *valerolactone* has been prepared.

When allyl-acetic acid, $CH_2{=}CH.CH_2.CH_2.CO_2H$, is brought in contact with hydrobromic acid, combination takes place, *γ*-brompentoic acid being formed, and this when heated with water is converted into valerolactone.[3] It may be obtained more readily by acting on *β*-acetylpropionic acid, $CH_3.CO.CH_2.CH_2.CO_2H$, with sodium amalgam and water.[4] It is a liquid possessing a weak but not unpleasant smell, boiling at 206°—207° and forming with water a neutral solution from which it may be withdrawn by ether. When boiled with baryta-water it yields barium oxypentoate, an amorphous substance like the similarly prepared calcium salt. *Silver pentoate*, $C_5H_9O_3Ag$, is somewhat difficultly soluble in cold, though readily soluble in boiling water, and it crystallizes in asymmetric prisms. Valerolactone has the following constitution:



In addition to this several other *lactones* are known. The lowest member of the series is the anhydride of *γ*-oxybutyric acid, a body which has already been described (p. 169). The general formula of these bodies is



[1] Ceresole, *Ber. Deutsch. Chem. Ges.* xv. 1326 and 1871.
[2] Gustin, *Bull. Soc. Chim.* lxxiii. 3.
[3] Messerschmidt, *Ann. Chem. Pharm.* ccviii. 92.
[4] Wolff, *ib.* ccviii. 104.

in which X signifies hydrogen or an alcohol radical. None of the acids corresponding to these lactones are known in the free state, but their salts are known, from which acids liberate the lactone.[1]

630 *β-Acetylpropionic Acid*, $CH_3.CO.CH_2.CH_2.CO_2H$, was first prepared by Tollens and A. v. Grote by boiling cane-sugar with dilute sulphuric acid, and termed by him *lævulinic acid*.[2] Conrad then showed that this same acid is obtained by the decomposition of ethyl aceto-succinate with baryta-water:[3]

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH.CO.OC_2H_5 \\ | \\ CH_2 \\ | \\ CO.OC_2H_5 \end{array} + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH. \end{array} + CO_2 + 2HO.C_2H_5.$$

Lævulinic acid is also easily formed when lævulose (lævo-rotatory grape-sugar) is boiled with dilute sulphuric acid or hydrochloric acid. In place of this sugar, such carbo-hydrates may be employed as yield this body on treatment with dilute acids.[4] Milk-sugar and dextro-rotatory grape-sugar (dextrose) are, however, on the other hand only converted with difficulty into this acid.[5] Formic acid is always formed together with the above acid:

$$C_6H_{12}O_6 = C_5H_8O_3 + CH_2O_2 + H_2O.$$

A part of the sugar is, in this reaction, converted into a brown humus-like body, so that in the most favourable cases 100 parts of cane-sugar yield 14 parts of lævulinic acid.[6] Usually, however, a much smaller yield is obtained (Grote, Kehrer and Tollens).

Lævulinic acid is easily soluble in water, alcohol, and ether, and crystallizes in scales melting at 33°·5. It is very hygroscopic, and traces of moisture lower its boiling point. Its specific

[1] Fittig, *Ann. Chem. Pharm.* ccviii. 111.
[2] *Ann. Chem. Pharm.* clxxv. 181; see also Grote, Kehrer and Tollens, *ib.* ccvi. 207.
[3] *Ib.* clxxxviii. 222.
[4] Bente, *Ber. Deutsch. Chem. Ges.* viii. 416; ix. 1157.
[5] Grote and Tollens, *Ann. Chem. Pharm.* ccvi. 226; Rodewald and Tollens, *ib.* ccvi. 23.
[6] Conrad, *Ber. Deutsch. Chem. Ges.* xi. 2178.

gravity is 1·135 at 15°, and it boils with slight decomposition at 239°. When heated with hydriodic acid and amorphous phosphorus,[1] or treated with sodium amalgam in acid solution,[2] it is reduced to normal pentoic acid. On oxidation with dilute nitric acid it yields succinic acid, acetic acid, oxalic acid, and carbon dioxide, and in addition hydrocyanic acid and ammonia.[3]

631 The lævulinates of the alkali metals are very soluble in water. The barium salt is amorphous.

*Calcium Lævulinate*, $(C_5H_7O_3)_2Ca$, crystallizes from water in easily soluble needles having a silky lustre.

*Zinc Lævulinate*, $(C_5H_7O_3)_2Zn$, forms silver-white needles or scales, which are easily soluble in water and alcohol.

*Silver Lævulinate*, $C_5H_7O_3Ag$, is difficultly soluble in cold water, more soluble in hot water, and crystallizes in long six-sided tables.

The ethereal salts of lævulinic acid are liquids which have a fruit-like smell. The following have been prepared (Grote, Kehrer and Tollens):

| | B.P. | Sp. Gr. at 0° |
|---|---|---|
| Methyl lævulinate, $C_5H_7(CH_3)O_3$ | 191°·5 | 1·0684 |
| Ethyl lævulinate, $C_5H_7(C_2H_5)O_3$ | 200°·5 | 1·0325 |
| Propyl lævulinate, $C_5H_7(C_3H_7)O_3$ | 215°·5 | 1·0103 |

*a-Trichloroxypentoic Acid*, $CH_3.CCl_2.CHCl.CH(OH).CO_2H$. The nitril of this acid is formed by the union of butyl chloral (p. 166) with hydrocyanic acid. It crystallizes in laminæ, melting at 101°—102°, and is difficultly soluble in water, but dissolves readily in alcohol.[4] When heated with strong hydrochloric acid the oxyacid is obtained, which is scarcely soluble in cold water, but is readily soluble in alcohol and ether. It crystallizes in gypsum-like tables which melt at 140°. When the alcoholic solution is saturated with hydrochloric acid, the ethyl salt is obtained, crystallizing in long prisms melting at 40° and boiling with slight decomposition at 255°.

[1] Kehrer and Tollens, *Ann. Chem. Pharm.* ccvi. 233.
[2] Fittig, *ib.* ccviii. 109. [3] Tollens, *ib.* ccvi. 257.
[4] Bischoff and Pinner, *Ann. Chem. Pharm.* clxxix. 97; Pinner and Klein, *Ber. Deutsch. Chem. Ges.* xi. 1488.

## Dibasic Acids, $C_5H_8O_4$.

632 *Glutaric Acid*, $CO_2H.CH_2.CH_2.CH_2.CO_2H$, was first obtained by Dittmar by heating glutanic acid, $C_3H_5(OH)(CO_2H)_2$, (to be hereafter described) with hydriodic acid, and termed by him *desoxyglutanic acid*.[1] It is obtained synthetically when trimethylene bromide (p. 130) is heated with potassium cyanide and alcohol, and the product boiled with potash.[2] It is also formed when ethyl sodacetacetate, diluted with benzene, is treated with ethyl $\beta$-iodopropionate, when the ethyl salt of acetoglutaric acid is first formed, a slightly smelling oily liquid boiling at 271°—272°, and decomposed by caustic potash into glutaric and acetic acids and alcohol.[3]

Glutaric acid is easily soluble in water, alcohol, and ether, crystallizing in large monoclinic prisms melting at 97°·5, and boiling with slight decomposition at 302°—304°. Of its salts, *zinc glutarate*, $C_5H_6O_4Zn$, is specially characteristic. It crystallizes in needles and dissolves at 18° in 102 parts of water. When a saturated solution is heated, it separates out as a granular precipitate consisting of characteristic microscopic crystals.

The ethyl salt, $C_5H_6O_4(C_2H_5)_2$, is a liquid boiling at 236°·5—237°.

*Glutaric Anhydride*, $C_5H_6O_3$, is formed by heating the acid for some time, or by treating the silver salt with acetyl chloride. It crystallizes from ether in long needles which melt at 56°—57°, and boils with partial decomposition at 282°—287°.[4]

*Amidoglutaric Acid*, or *Glutaminic Acid*, $C_3H_5(NH_2)(CO_2H)_2$, is formed together with other compounds, when various albuminoid substances are boiled with dilute sulphuric acid,[5] or with hydrochloric acid and tin dichloride.[6] *Glutamine*, the corresponding homologous amide of asparagine, is found in beet-root,[7] in the shoots of vetch [8] and the pumpkin,[9] but has not been

[1] *Journ. Prakt. Chem.* [2], v. 338.
[2] Julie Lermontow and Markownikow, *Ann. Chem. Pharm.* clxxxii. 341; Reboul, *Ann. Chim. Phys.* [5], xiv. 501.
[3] Wislicenus and Limpach, *Ann. Chem. Pharm.* cxcii. 128.
[4] Markownikow, *Journ. Russ. Chem. Ges.* ix. 283.
[5] Ritthausen, *Journ. Prakt. Chem.* xcix. 454; ciii. 65 and 274; cvii. 208; [2], iii. 314.
[6] Hlasiwetz and Habermann, *Ann. Chem. Pharm.* clxix. 157.
[7] Schulze, *Ber. Deutsch. Chem. Ges.* x. 85.
[8] Gorup-Besanez, *ib.* x. 780.
[9] Schulze and Barbieri, *Journ. Prakt. Chem.* [2], xx. 391.

obtained in the pure state from these. It is converted by boiling with hydrochloric acid into glutaminic acid. Glutaminic acid crystallizes in rhombic pyramids or sphenoids. It dissolves at 16° in 100 parts of water, is less soluble in spirit of wine, and does not dissolve in absolute alcohol. Its salts crystallize well, and it also combines with acids.

633 *a-Oxyglutaric Acid*, or *Glutanic Acid*, $C_3H_5(OH)(CO_2H)_2$, was obtained by Ritthausen by the action of nitrous acid on glutaminic acid.[1] It is best to employ the hydrochlorate of this latter body, and to add the requisite quantity of potassium nitrite to its dilute solution, and, to complete the decomposition, nitrogen trioxide is led in. The liquid is evaporated on a water-bath, and the acid extracted with ether.[2] Oxyglutaric acid occurs in molasses, being probably a product of decomposition of the glutaminic acid contained in the sugar-cane.[3] It is easily soluble in water, and forms small crystals melting at 72°—73° and solidifying to a transparent mass. When the solution is neutralized with zinc carbonate and evaporated to a syrup, transparent four-sided tables separate out after a few days. These are converted by hot water into a difficultly soluble pulverulent salt which cannot be again transformed into the soluble variety, and which is deposited from hot saturated solution in warty concretions or small needles having the composition $C_5H_6O_5Zn + 3H_2O$.

*β-Oxyglutaric Acid*, $C_3H_5(OH)(CO_2H)_2$, was obtained by Simpson, who termed it *oxypyrotartaric acid*, by heating dichlorhydrin, $CH_2Cl.CH(OH).CH_2Cl$ (see Glycerine), with alcohol and potassium cyanide, and boiling the product with caustic potash. It forms crystals easily soluble in water, alcohol, and ether, and melting at 135°.[4] Its constitution is seen from its mode of formation, and as only two isomeric normal acids of this composition can exist, that of the *α*-acid is thus also determined:

*α*-Oxyglutaric Acid.

$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH_2 \\ | \\ CH(OH).CO_2H. \end{array}$$

*β*-Oxyglutaric Acid.

$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH(OH) \\ | \\ CH_2.CO_2H. \end{array}$$

[1] *Journ. Prakt. Chem.* ciii. 239.
[2] Markownikow, *Ann. Chem. Pharm.* clxxxii. 348.
[3] Von Lippmann, *Ber. Deutsch. Chem. Ges.* xv. 1156.
[4] *Proc. Roy. Soc.* xiii. 44.

634 *Pyrotartaric Acid*, or *Methylsuccinic Acid*, $CO_2H.CH(CH_3).CH_2.CO_2H$. The history of this acid is to be found under the heading of Pyroracemic Acid. It is formed together with this body and other products, in the dry distillation of tartaric acid and its isomerides, as well as when these are heated with concentrated hydrochloric acid to 180°.[1] Its formation probably precedes that of the pyroracemic acid, as this latter acid, which heated either by itself to 170°, or with hydrochloric acid to 100°,[2] also yields pyrotartaric acid. It is therefore also formed in the distillation of glyceric acid (p. 153). Simpson obtained it synthetically by heating propylene bromide with potassium cyanide and alcohol, and heating the *pyrotartronitril*, $CH_3.CH(CN).CH_2.CN$, thus obtained with fuming hydrochloric acid.[3] This nitril is a liquid which boils at 252°—254°, and on cooling crystallizes to colourless transparent prisms which melt at 12°.[4] Wislicenus prepared this acid from β-brombutyric acid by heating the ethyl salt with potassium cyanide, and boiling the product with caustic potash.[5] Conrad then showed that it is formed when ethyl sodacetacetate is treated with ethyl α-brompropionate, when *ethyl β-methylacetosuccinate*, boiling at 259°, is formed, and this is decomposed by caustic potash into pyrotartaric acid.[6] It was obtained in the same way from *ethyl α-methylacetosuccinate*, $CH_3C(CO.CH_3)(CO_2.C_2H_5)CH_2.CO_2.C_2H_5$, a liquid boiling at 263°, and obtained by the action of methyl iodide on ethyl sodacetosuccinate.[7]

In order to prepare pyrotartaric acid, a mixture of tartaric acid and powdered pumice-stone [8] is distilled in the following way: 400 grams of tartaric acid are kept for 15—20 minutes in a state of fusion and then more strongly heated until acid vapours are evolved, mixed with 400 grams of hot pumice powder, and then the whole slowly distilled in a retort, the operation lasting 8 or 9 hours.[9] The distillate is then dissolved in 3 to 4 times its bulk of water, and separated from the oily products by means of a moistened filter. The liquid is then evaporated on a water-bath and the coloured acid is recrystallized from dilute nitric

[1] Geuther and Riemann, *Zeitsch. Chem.* 1869, 318.
[2] Clermont, *Ber. Deutsch. Chem. Ges.* vi. 92; Böttinger. *ib.* ix. 837 and 1823.
[3] *Phil. Trans.* 1861, part i. p. 61; see also Claus, *Ann. Chem. Pharm.* cxci. 37.
[4] Pinner, *Ber. Deutsch. Chem. Ges.* xii. 2053.
[5] *Ann. Chem. Pharm.* clxv. 93.
[6] *Ann. Chem. Pharm.* clxxxviii. 227.
[7] Kressner, *ib.* cxcii. 138.
[8] Arppe, *Ann. Chem. Pharm.* lxvi. 73.
[9] Béchamp, *Compt. Rend.* lxx. 1000.

acid. The difficultly soluble acid potassium pyrotartrate is prepared from the mother-liquors, recrystallized from weak alcohol, decomposed by sulphuric acid, and the pyrotartaric acid extracted with ether.[1]

If tartaric acid be dissolved in an equal volume of acetic acid and evaporated over a naked flame until it becomes syrupy, and this allowed to stand, pyrotartaric acid crystallizes out in a few days.[2] If india-rubber be boiled with caustic potash, amongst other acids which are formed, 8 per cent. of pyrotartaric acid is obtained.[3] Pyrotartaric acid crystallizes in small triclinic prisms which are grouped in stellar masses or warty concretions. It dissolves at 20° in 1·5 parts of water, and is also easily soluble in alcohol and ether. It has a cool purely acid taste, melts at 112°, and decomposes, when quickly heated above 200°, into water and the anhydride. If, however, it be exposed for a long time to a temperature of 200°—210° small quantities of butyric acid and carbon dioxide are also formed.[4] The latter products of decomposition are given off when the aqueous solution is exposed to sunlight in the presence of a uranic salt.[5]

635 *Normal Potassium Pyrotartrate,* $C_5H_6O_4K_2 + 2H_2O$, is very easily soluble in water and crystallizes in flat prisms, which on exposure to dry air lose one molecule of water and are converted into warty masses consisting of microscopic needles.

*Acid Potassium Pyrotartrate,* $C_5H_6O_4KH$, is precipitated from the saturated solution of the foregoing salt by the acid in the form of a crystalline powder. It crystallizes from hot water in large transparent monoclinic prisms.

*Normal Calcium Pyrotartrate,* $C_5H_6O_4Ca + 2H_2O$, crystallizes in microscopic four-sided prisms which dissolve in about 100 parts of boiling water. If dissolved in the aqueous acid and the solution carefully evaporated, crystals of the compound $(C_5H_7O_4)_2Ca + 4C_5H_8O_4 + 4H_2O$ are deposited.[6]

*Normal Lead Pyrotartrate,* $C_5H_6O_4Pb + 2H_2O$, is very slightly soluble in cold water but dissolves more readily in boiling water and crystallizes in prisms.

*Silver Pyrotartrate,* $C_5H_6O_4Ag_2$, is a slimy precipitate, slightly soluble in hot water; it dissolves more readily in ammonia, from which it crystallizes in needles.

[1] Bourgoin, *Ann. Chim. Phys.* [5], xii. 419.
[2] Sacc, *Zeitsch. Chem.* 1870, 432.
[3] Barth and Hlasiwetz, *Ann. Chem. Pharm.* cxxxviii. 73.
[4] Claus, *Ann. Chem. Pharm.* cxci. 48. [5] Seekamp, *ib.* cxxxiii. 253.
[6] Arppe, *Ann. Chem. Pharm.* lxvi. 73, xc. 138.

The solutions of the normal salts are precipitated with ferric chloride.

*Ethyl Pyrotartrate*, $C_5H_6O_4(C_2H_5)_2$, is an oily liquid boiling with decomposition at 218°, possessing a burning bitter taste, and smelling like sweet flag.[1]

*Pyrotartaric Anhydride*, $C_5H_6O_3$, is best obtained by heating the acid with phosphorus pentoxide.[2] It is an oily liquid boiling at 245° and is slowly dissolved by water.

*Oxypyrotartaric Acid*, or *α-Methoxysuccinic Acid*, $C_5H_7(OH)O_4$. This acid is formed when ethyl acetacetate is heated for 3 days with anhydrous hydrocyanic acid and the product boiled with hydrochloric acid:

$$\begin{array}{l} CH_3 \\ | \\ C(OH)CN \\ | \\ CH_2.CO.OC_2H_5 \end{array} + HCl + 3H_2O = \begin{array}{l} CH_3 \\ | \\ C(OH)CO.OH + \\ | \\ CH_2.CO.OH \end{array}$$

$$NH_4Cl + HO.C_2H_5.$$

If the solution be allowed to evaporate over sulphuric acid, needles united in stellar groups are deposited. These melt at 108°, are very deliquescent, and also easily soluble in alcohol and ether. When heated to 200° they decompose mainly into water and citraconic anhydride, a body which, together with various isomeric oxypyrotartaric acids, will be described under the head of Citric Acid.

636 *Ethyl Malonic Acid*, $CH_3.CH_2.CH(CO_2H)_2$. When the ethyl salt of *α*-brombutyric acid is heated with potassium mercuric cyanide to 130° the corresponding salt of *α*-cyanbutyric acid is obtained. This is an aromatic smelling liquid boiling at 209°, and on heating with hydrochloric acid or caustic potash is converted into ethyl malonic acid.[3] This acid is easily soluble in water, alcohol, or ether, and crystallizes in rhombic prisms which melt at 111°·5 and decompose at 160° into carbon dioxide and butyric acid. Its calcium salt, $C_5H_6O_4Ca+H_2O$, crystallizes in prisms and dissolves more readily in cold than in hot water. Solutions of its normal salts are not precipitated by ferric chloride.

[1] Gruner, *Neu Journ. Pharm.* xxiv. 55 ; Malaguti, *ib.* xxv. 272 ; Arppe, *loc. cit.*

[2] Demarçay, *Bull. Soc. Chim.* [2], xxvii. 120 ; Morris, *Journ. Chem. Soc.* 1880, i 6.

[3] Wislicenus and Urech, *Ann. Chem. Pharm.* clxv. 93 ; Tupolew, *ib.* clxxi. 28 ; Markownikow, *ib.* clxxxii. 329.

The ethyl salt was obtained by Markownikow by the action of ethyl iodide on the silver salt, and Conrad prepared it from ethyl malonate by adding 16 grams of this substance and 20 grams of ethyl iodide to a solution of 2·3 parts of sodium in 25 grams of absolute alcohol, and then isolated the ethereal salt by fractional distillation. It is a mobile liquid which boils at 207° and at 18° has a specific gravity of 1·008.[1] When acted upon by chlorine it is converted into the *ethyl salt of ethyl chlormalonic acid*, $CH_3.CH_2.CCl(CO_2C_2H_5)_2$, a liquid boiling at 228°.

*Ethyl Oxymalonic Acid*, or *Ethyl Tartronic Acid*, $CH_3CH_2.C(OH)(CO_2H)_2$, is formed by heating the chlorinated ethereal salt with baryta-water. It is crystalline, soluble in water, and melts at 98°, decomposing at 180° into carbon dioxide, and *a*-oxybutyric acids, products which are also formed when the chlorinated ethereal salt is boiled for some time with dilute hydrochloric acid in connection with an inverted condenser.[2]

*Dimethyl Malonic Acid*, $(CH_3)_2C(CO_2H)_2$, was obtained by Markownikow by heating the ethyl salt of bromisobutyric acid with water and cyanide of potassium. The product is then treated with sulphuric acid and the impure cyanisobutyric acid extracted by ether and decomposed by potash. The solution is then evaporated and after acidification treated with ether.[3]

Dimethyl malonic acid is somewhat less easily soluble in water than its isomeric acids, and is difficultly soluble in alcohol. It crystallizes in four-sided prisms which sublime in feather-like needles at about 120° and melt at 170°, when decomposition into carbon dioxide and isobutyric acid occurs. Its calcium salt is easily soluble in cold water, and separates out on warming.

[1] *Ann. Chem. Pharm.* cciv. 134.
[2] Guthzeit, *Ber. Deutsch. Chem. Ges.* xiv. 618. *Ann. Chem. Pharm.* ccix. 232.
[3] *Ann. Chem. Pharm.* clxxxii. 336.

## THE HEXYLENE COMPOUNDS.

637 *Normal Hexylene*, $C_6H_{12}$, can exist in three isomeric forms:

Butyl-ethylene, $CH_3.CH_2.CH_2.CH_2.CH = CH_2$.
Methyl-propyl-ethylene, $CH_3.CH_2.CH_2.CH = CH.CH_3$.
Diethyl-ethylene, $CH_3.CH_2.CH = CH.CH_2.CH_3$.

Of these only the second is known with certainty. This is easily obtained by heating secondary hexyl iodide with alcoholic potash.[1] It is a liquid possessing a faint garlic-like smell, boiling under a pressure of 737°·9 at 67°, and having at 0° a specific gravity of 0·6997. If dissolved in a mixture of 1 volume of water and 3 volumes of sulphuric acid, and if water be then added, methyl-butyl carbinol separates out. It easily unites with hydriodic acid to form the corresponding iodide, and also combines slowly in the cold with hydrochloric acid to form secondary hexyl chloride. It is converted by oxidation into butyric and acetic acids.[2]

An hexylene possessing the same composition is obtained when the mixture of monochlorides obtained from the normal hexane derived from mannite is heated with potash and alcohol. At the same time a mixture of methyl hexyl ethers is obtained.[3] On the other hand, hexane from petroleum yields together with the ethers a mixture of two hexylenes, one of which unites with hydrochloric acid to form a hexyl chloride boiling at 116°—118°, the alcohol of which yields acetic and propionic acids on oxidation. This would show that a normal paraffin is mixed with the hexane. The second hexylene does not combine with hydrochloric until it is heated to 130°—140°, but the hexyl

[1] Erlenmeyer and Wanklyn, *Ann. Chem. Pharm.* cxxxv. 141; Hecht, *ib.* clxv. 150.
[2] Hecht, *Ber. Deutsch. Chem. Ges.* xi. 1152; Domac, *Monatsh. Chem.* ii. 309.
[3] Schorlemmer, *Proc. Roy. Soc.* xxix. 364.

chloride thus obtained is identical with that got from mannite.[1] Probably this hexylene is the isomeric butyl-ethylene.

Two hexylenes have been found in the products of the distillation of pitch from Pechelbronn, possessing the same properties as those from petroleum.[2]

*Methyl-propyl-ethylene Glycol*, $C_6H_{12}(OH)_2$. This was first obtained by Wurtz by the same process as ethylene glycol.[3] It is also formed by heating the bromide with dilute solution of carbonate of potash,[4] or with dilute sulphuric acid.[5] It is a thick liquid soluble in water, boiling at 207°, and having at 0° a specific gravity of 0·9669. On oxidation it yields the same products as the olefine. When heated with hydrochloric acid it forms the chlorhydrin, which is also produced by the union of hexylene with hypochlorous acid. This is a heavy colourless liquid which decomposes on heating. Nascent hydrogen converts it into methyl-butyl carbinol (Domac). Hence its constitution is $C_3H_7.CHCl.CH(OH)CH_3$. When distilled with caustic potash it yields hexylene oxide, $C_6H_{12}O$, a light pleasantly smelling liquid boiling at 115° (Wurtz).

*Hexylene Bromide*, $C_6H_{12}Br_2$, is a strongly smelling oily liquid, boiling at 195°—197°, and having a specific gravity at 0° of 1·6058.[6] When heated with potash and alcohol *bromhexylene*, $C_6H_{11}Br$, is formed, a liquid boiling at 138°—141°, and having a specific gravity at 0° of 1·2205.

*α-Ethyl-dimethyl-ethylene*, $C_2H_5(CH_3)C=CH.CH_3$, is formed as a by-product in the preparation of diethyl-methyl-carbinol, and also when its iodide is decomposed with alcoholic potash:

$$\begin{array}{l} CH_3.CH_2\diagdown \\ CH_3.CH_2\!-\!Cl \\ \quad\quad CH_3\diagup \end{array} \;=\; \begin{array}{l} CH_3.CH_2\diagdown \\ CH_3.CH\!=\!C \\ \quad\quad CH_3\diagup \end{array} \;+\; HI.$$

It is a liquid boiling at 69°·5—71°, and having a specific gravity at 0° of 0·698. On oxidation it yields acetic acid and ethyl-methyl ketone.[7]

*β-Ethyl-dimethyl-ethylene*, $C_2H_5.C\equiv C(CH_3)_2$, is obtained in the preparation of dimethyl-propyl-carbinol as well as by the

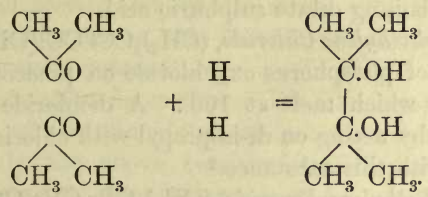
[1] Morgan, *Journ. Chem. Soc.* N.S. xiii. 301; clxxvii. 304; Schorlemmer, *ib.* 306.
[2] Le Bel, *Bull. Soc. Chim.* xviii. 167.
[3] *Ann. Chim. Phys.* [4], iii. 180.
[4] Hecht and Munier, *Ber. Deutsch. Chem. Ges.* xi. 1154.
[5] Hecht, *ib.* xi. 1423.
[6] Hecht and Strauss, *Ann. Chem. Pharm.* clxxii. 62.
[7] Tchaikowsky, *Jahresb.* 1872, 350; Jawein, *Ann. Chem. Pharm.* cxcv. 259.

action of caustic potash on the iodide. It boils at 65°—67°, and at 0° has a specific gravity of 0·702. On oxidation it yields acetone and acetic and propionic acids.[1]

*Pseudo-butyl-ethylene*, $(CH_3)_3C.CH{=}CH_2$, is formed by heating pinacolyl iodide (Part I. p. 633,) with water. It is a liquid boiling at 70°, and with bromine forming a crystalline dibromide.[2]

*Tetramethyl-ethylene*, $(CH_3)_2C{=}C(CH_3)_2$, is formed by acting with alcoholic potash on the iodide of isopropyl-dimethyl-carbinol. It is a liquid boiling at 73°, and having a specific gravity at 0° of 0·712.[3] On oxidation it yields acetone, together with acetic acid and tertiary valeric acid.

638 *Tetramethyl-ethylene Glycol*, $(CH_3)_2C(OH).C(OH)(CH_3)_2$, was prepared by Fittig by acting with sodium on acetone, and termed paracetone.[4] Städeler, who investigated it more exactly, gave to it the name of *pinacone*, which it now usually bears (from πίναξ, a tablet), because it unites with water to form a compound crystallizing in large tablets.[5] Friedel then showed that it is formed (together with isopropyl alcohol) by the action of sodium amalgam on an aqueous solution of acetone.[6]



That it is obtained by the action of sodium alone, without any addition of water, is accounted for by the fact that a part of the acetone is converted into mesityl oxide and phorone with separation of water (see Part I., pp. 572, 573).

Its formation from acetone renders it very probable that it is a glycol of tetramethyl-ethylene, and this is further proved by the fact that it is also formed when the dibromide of this olefine is treated with silver acetate, and the diacetate then decomposed by baryta.[7] In order to prepare it a solution of carbonate of potash is made of such a strength that it does not perceptibly dissolve any acetone, but readily evolves hydrogen when sodium is added.

[1] Jawein, *Ann. Chem. Pharm.* cxcv. 255.
[2] Friedel and Silva, *Jahresb.* 1873, 339.
[3] Pawlow, *Ann. Chem. Pharm.* cxcvi. 124.
[4] *Ann. Chem. Pharm.* cx. 25; cxiv. 54.
[5] *Ann. Chem. Pharm.* cxi. 277.
[6] *Ib.* cxxiv. 329.
[7] Pawlow, *Ann. Chem. Pharm.* cxcvi. 126.

To this is added three parts of acetone, and one part of sodium is gradually introduced in large pieces. The product is then separated by distillation into isopropyl alcohol and pinacone.[1]

This latter compound is contained in the product as the above-mentioned hydrate which decomposes by repeated fractional distillation into water and the glycol, which is a syrupy colourless liquid having at 15° a specific gravity of 0·96, and boiling at 176°—177°. It does not solidify at 0°, but when placed in a dry atmosphere it passes into a snow-white crystalline mass. This solid modification melts at 35°—38°, and boils at 171°—172°. The distillate soon solidifies again. It is easily soluble in alcohol and ether, and crystallizes from boiling sulphide of carbon in small needles.[2] It dissolves sparingly in cold and more readily in boiling water, and on cooling, *pinacone hydrate*, $C_6H_{14}O_2 + 6H_2O$, deposits in large four-sided tables which melt at 46°·5, and sublime at the ordinary temperature, volatilizing readily in a current of steam. On oxidation with chromic acid solution, pinacone first passes into acetone, and it is converted into pinacoline (Part I., p. 633) by the action of boiling dilute sulphuric acid.

*Tetra-methyl-ethylene Chloride*, $(CH_3)_2CCl.CCl(CH_3)_2$, is formed by the action of phosphorus oxychloride on pinacone. It forms white crystals which melt at 160°. A dichloride obtained by Schorlemmer by acting on di-isopropyl with chlorine appears to be identical with this substance.[3]

*Tetramethyl-ethylene Bromide*, $(CH_3)_2CBr.CBr(CH_3)_2$, is easily formed by the union of bromine with the olefine. It crystallizes from ether in large well-formed needles which melt with decomposition above 140° (Pawlow).

## OXYACIDS, $C_6H_{12}O_3$, AND KETONIC ACIDS, $C_6H_{10}O_3$.

639 *Oxycaproic Acid*, or *Leucic Acid*, $CH_3(CH_2)_3.CH(OH).CO_2H$, was first discovered by Strecker by the action of nitrous acid on the corresponding amido-acid or leucine.[4] It was afterwards investigated by Waage [5] and Thudichum.[6] It is easily soluble in water, alcohol, and ether, crystallizes in needles or prisms,

[1] Friedel and Silva, *Jahresb.* 1873, 340.
[2] Linnemann, *Ann. Chem. Pharm.* Suppl. iii. 374.
[3] Friedel and Silva, *Ber. Deutsch. Chem. Ges.* vi. 35.
[4] *Ann. Chem. Pharm.* lxviii. 55 ; see also Gössmann, *ib.* xci. 135.
[5] *Ib.* cxviii. 295. [6] *Quart. Journ. Chem. Soc.* xiv. 307.

melts at 73°, and begins to sublime at 100°. When heated for some time it is converted into the anhydride, a syrup insoluble in water.

Its salts as a rule crystallize well. *Zinc leucate*, $(C_6H_{11}O_3)_2Zn + H_2O$, forms colourless plates, and dissolves at 16° in 300 parts of water; it is rather more soluble in boiling water, and still more soluble in alcohol. *Copper lecucate*, $(C_6H_{11}O_3)_2Cu$, is also difficultly soluble in water, and crystallizes from alcohol in light blue plates. *Silver leucate*, $C_6H_{11}O_3Ag$, is deposited from hot water in colourless crystals.

*Amidocaproic Acid*, or *Leucine*, $C_5H_{10}(NH_2).CO_2H$, was first prepared by Proust, in 1818, from decomposing cheese, and described by him as "oxide caséeux."[1] Two years afterwards, Braconnot, by the action of sulphuric acid on muscular fibre, glue, and other animal substances, obtained, together with glycocoll ("sucre de gelatine" or amidoacetic acid) "une matière blanche particulière," which he termed *leucine*, from λευχος, white.[2] Mulder then showed, in 1838, that leucine is identical with Proust's compound, and that it not only is formed in the putrefaction of casein, and by the action of sulphuric acid on albumen, muscular tissue, etc., but also when these bodies are heated with caustic potash.[3]

Later investigations have shown that all substances belonging to the group of albuminoids or other nearly-related substances yield not only the above two amido-acids but a third to which the name of *tyrosine* or *oxyphenylamidopropionic acid*, $C_6H_4(OH)C_2H_3(NH_2)CO_2H$, is given; and that leucine frequently occurs either as a normal or pathological product of metabolism.[4] It has been found in the liver, spleen, pancreas, lungs, &c., as well as in the lower forms of animal life, such as crayfish, spiders, caterpillars, pupæ of butterflies, &c. According to Gorup-Besanez it also occurs in the vegetable kingdom, and, together with asparagin (amidosuccinamic acid), in the white sprouts of vetch. He showed also that the substance found by Reinsch in *Chenepodium album*, is, in fact, leucine.[5] Schulze and Barbieri found it, together with tyrosine, aspartic and glutamic acids, in the pumpkin.[6] These different amido-

[1] *Ann. Chim. Phys.* x. 40.
[2] *Ann. Chim. Phys.* xiii. 119.
[3] *Journ. Prakt. Chem* xvi. 290.
[4] Frerichs and Städeler, *Jahresb.* 1856, 702; Gorup-Besanez, *Ann. Chem. Pharm.* xcviii. 1; Cloëtta, *ib.* xcix. 289; Städeler, *ib.* cxvi. 60.
[5] *Ber. Deutsch. Chem. Ges.* vii. 146, 569; see also Cossa, *ib.* viii. 1357.
[6] *Ib.* xi. 1233.

acids also occur in yeast, having their origin, as in other cases, in the decomposition of albuminoids.

*Preparation.* Clippings of horn serve as a convenient material for the preparation of leucine.[1] According to Schwanert one kilogram of this is boiled with a mixture of 2½ kilos. of sulphuric acid and 6½ kilos. of water for twenty-four hours, the evaporated water being from time to time replaced. The hot liquid is then neutralized with lime, filtered, and evaporated down to 6 kilos., the lime contained in the liquid precipitated with oxalic acid, and the residue concentrated in order to allow the leucine and tyrosine to crystallize out. The latter substance is more difficultly soluble than leucine. It is, therefore, separated by recrystallization, and the leucine purified by crystallization from alcoholic ammonia (Huppert). The yield is about 10 per cent. of the weight of the horn. A larger yield may be obtained from the cervical ligament of the ox. This is boiled out with dilute acetic acid, dried at 100°, and then boiled for three hours with a mixture of two parts of sulphuric acid and three parts of water; the yield amounts to from 36 to 45 per cent. of the dried substance.[2]

640 *Properties.* Leucine dissolves in 48·8 parts of water at 12° (Hüfner), and is more soluble in hot water, but is only very slightly soluble in alcohol and insoluble in ether. It crystallizes in thin pearly nacreous laminæ or scales which are wetted by water with difficulty. If not perfectly pure it separates out in concentric nodules which are seen to consist of concentrically grouped, highly-refracting needles, having under the microscope the appearance shown in figs. 108 and 109. When carefully heated in a tube open at both ends, it sublimes in light flocks resembling zinc oxide (lana philosophica) obtained by burning the metal in the air. Sublimed leucine consists of very thin scales massed together in a rosette-like form as shown in fig. 110. When leucine is heated in a retort it melts at 170° to form a light brown sticky mass which decomposes at 180°, yielding chiefly pentylamine and carbon dioxide. If fused with caustic potash, pentoic acid, hydrogen, ammonia, and carbon dioxide are obtained (Liebig); and when heated with fuming hydriodic acid to 140° it is converted into caproic acid and ammonia.[3] A characteristic reaction for leucine is that when heated with nitric acid on platinum foil a colourless residue is left which is coloured yellow

[1] Hinterberger, *Ann. Chem. Pharm* lxxi. 72.
[2] Erlenmeyer and Schölfer, *Jahresb.* 1859, 596.
[3] Hüfner, *Zeitsch. Chem.* 1868, 391.

on addition of caustic soda, and on careful evaporation this forms an oily drop which does not wet the platinum.[1] An apueous solution of leucine is coloured deep red by ferric chloride. Like glycocoll it forms easily soluble salts with acids, and combines with the nitrates of silver, calcium, magnesium, &c.

FIG. 108.

FIG. 109.

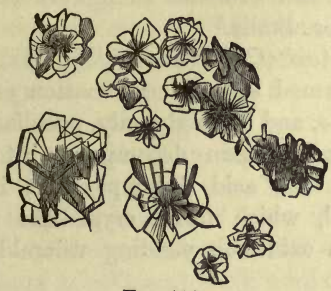


FIG. 110.

Amongst its metallic compounds the copper salt is the most characteristic.

*Copper Amidocaproate*, $[C_5H_{10}(NH_2)CO_2]_2Cu$, is obtained by dissolving copper hydroxide in a boiling solution of leucine. It forms light blue scales dissolving in 3045 parts of cold and 1460 parts of boiling water.[2]

[1] Scherer, *Jahresb.* 1857, 541.
[2] Hofmeister, *Liebig's Ann.* clxxxix. 16.

641 According to Hüfner leucine can be obtained from normal caproic acid, by converting into the monobrominated acid, and heating this with ammonia. On careful comparison no difference could be observed between this artificial and the natural leucine.[1] Nevertheless, they do not appear to be identical, for when monobromcaproic acid is heated with a solution of carbonate of soda it yields an *oxycaproic acid* different from leucic acid. This oxycaproic acid forms a stellated or nodular crystalline mass, and melts at 60°—62°. Chromic acid solution oxidizes it to pentoic acid. *Zinc oxycaproate,* $(C_6H_{11}O_3)_2Zn + 2H_2O$, is a flocculent precipitate which dissolves at 16° in 681 parts of water, and crystallizes from alcohol in fine silky needles. The other salts of this acid differ from the corresponding leucates.[2] The cause of the isomerism of these two acids has yet to be explained.

*Leucinimide,* $C_4H_9CH.CO$ (NH). This body occurs, together with leucine and the above-named amido-acids as a product of decomposition of the albuminoids.[3] It was first observed by Bopp,[4] who, however, did not investigate it further. It crystallizes in microscopic rhombic needles difficultly soluble in boiling and insoluble in cold water, but soluble in cold alcohol. On heating it melts, and sublimes in light flocculæ and it is unaltered by acids or alkalis.[5]

*Oxyisocaproic Acid,* $(CH_3)_2CH.CH_2CH(OH).CO_2H$. The nitril of this acid is formed by the combination of hydrocyanic acid and valeraldehyde, and is a light, oily, peculiarly-smelling liquid, which when heated again decomposes into its constituents. Fuming hydrochloric acid decomposes it into sal-ammoniac and the oxyacid, which forms crystalline scales, melting at 54°—55°, and on oxidation yielding valeraldehyde and valeric acid.[6]

*Amido-isocaproic Acid,* or *Isoleucine,* $(CH_3)_2CH.CH_2.CH(NH_2)CO_2H$. This body was obtained by Limpricht by acting with hydrocyanic and hydrochloric acids on valeraldehyde-

[1] *Journ. Prakt. Chem.* [2], i. 6.
[2] Jelisafow and Beilstein, *Org. Chem.* 435.
[3] Hesse and Limpricht, *Ann. Chem. Pharm.* cxvi. 201; Erlenmeyer, *ib.* cxix. 17; Hlasiwetz and Habermann, *ib.* clix. 328.
[4] *Ib.* lxix. 20.
[5] Thudichum, *Journ. Chem. Soc.* [2], viii. 409.
[6] Erlenmeyer and Sigel, *Ber. Deutsch. Chem. Ges.* vii. 1109; Ley, *ib.* x. 231.

ammonia.[1] In order to prepare it, two parts of the latter compound, which must be pure, and one part of aqueous hydrocyanic acid are allowed to stand overnight, and then an excess of hydrochloric acid added, and the whole boiled for some time.[2] Isoleucine closely resembles leucine, the compounds of these two bodies being so similar that the former substance was for a long time considered to be leucine. It is distinguished, however, from the latter body, inasmuch as at 12° it requires for solution 117·5 parts of water.

*Isoleucinimide* $(CH_3)_2CH.CH_2.CH.CO$ (NH), is formed, when the foregoing compound is heated in a current of hydrochloric acid to 220°—230°.[3] It crystallizes from hot alcohol in fine needles which, when heated, sublime in flocks without melting. It is scarcely soluble, even on boiling, in water, ammonia, caustic potash, or dilute acids.

642 *Diethyl-oxyacetic Acid,* $(C_2H_5)_2C(OH).CO_2H$. This acid, which was formerly believed to be leucic acid, and is usually called *diethyl-oxalic acid*, was discovered by Frankland[4] and investigated by himself and Duppa.[5] Its ethyl salt is formed by the action of zinc-ethyl on ethyl oxalate. Instead of zinc-ethyl, ethyl iodide and zinc may also be used. The metal should in this case be slightly amalgamated by dipping it for a short time in a weak solution of corrosive sublimate.[6] All the materials used must, of course, be anhydrous. To 191 grams of ethyl oxalate 409 grams of ethyl iodide are taken together with an excess of zinc, and to this about 5 grams of zinc-ethyl and 10 grams of ether are added, by which means the action is accelerated, and a better yield is obtained. The action is not assisted when a larger quantity of zinc-ethyl is used.[7] The mixture is heated in the water-bath to 60°—70°, until after a lapse of 12-15 hours a yellowish thick semi-crystalline mass is formed. The following represents the reaction:

$$\begin{matrix} CO.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{matrix} + 2Zn\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} = \begin{matrix} C_2H_5\ C_2H_5 \\ \diagdown\ \diagup \\ C—O—ZnC_2H_5 \\ | \\ CO.OC_2H_5. \end{matrix} + Zn\begin{matrix} C_2H_5 \\ OC_2H_5. \end{matrix}$$

[1] *Ann. Chem. Pharm.* xciv. 243. [2] Hüfner, *Journ. Prakt. Chem.* [2], i. 6.
[3] Kohler, *Ann. Chem. Pharm.* cxxxiv. 367.
[4] *Proc. Roy. Soc.* xii. 396. [5] *Ib.* xiv. 17; *Chem. Soc. Journ.* [2], iii. 133.
[6] Fittig, *Ann. Chem. Pharm.* cc. 21.
[7] Chapman and Smith, *Journ. Chem. Soc.* [2], v. 173.

If water be added to the product of this reaction, ethane is evolved, and the ethereal salt of diethyl oxalic acid separates out:

$$\begin{array}{l} C_2H_5\ CH_5 \\ \diagdown\ \diagup \\ C\text{—}O\text{—}ZnC_2H_5 \\ | \\ CO.OC_2H_5 \end{array} + 2H_2O = \begin{array}{l} C_2H_5\ C_2H_5 \\ \diagdown\ \diagup \\ C.OH \\ | \\ CO.OC_2H_5. \end{array} + C_2H_6 + Zn(OH)_2.$$

The ethereal salt is distilled off in a current of steam and purified by fractional distillation. In order to obtain the free acid the salt is heated with baryta solution, and the baryta-salt precipitated with dilute sulphuric acid. The free acid is also obtained by heating the ethereal salt with hydrochloric acid to 110°. This dissolves in 2·85 parts of water at 17°·5,[1] and forms triclinic saponaceous crystals which, according to Duppa and Frankland, melt at 74°·5, and according to Haushofer at 80°,[2] but begin to sublime at 50°. Chromic acid solution oxidizes this substance to diethyl-ketone, carbon dioxide, and water (Chapman and Smith).

The most characteristic of the salts is *zinc diethyl-oxyacetate* $(C_6H_{11}O_3)_2Zn$, crystallizing in needles or scales, dissolving at 16° in 301 parts of water, and therefore possessing the same solubility at this temperature as zinc leucate. But whilst the latter salt is more easily soluble in boiling water, the reverse is the case with the salt just described.

643 *Ethyl Diethyl-oxyacetate* $(C_2H_5)_2C(OH).CO.OC_2H_5$. This is a colourless oily liquid, boiling at 175°, having a specific gravity at 18°·7 of 0·9613, whilst that of its vapour is 5·36. It possesses a sharp taste and a penetrating ethereal smell. It is formed by the reactions just described, and also when zinc-ethyl acts upon the chloride of ethyl-oxalic acid and the product is heated with water.[3] Frankland and Duppa have also described the following ethers:

| | B.P. | Sp. Gr. | at |
|---|---|---|---|
| Methyl diethyl-oxyacetate, $C_6H_{11}O_3.CH_3$ | 165° | 0·9866 | 16°·5 |
| Amyl diethyl-oxyacetate, $C_6H_{11}O_3.C_5H_{11}$ | 225° | 0.9323 | 13° |

Other bodies belonging to the group of the oxycaproic acids will be afterwards described.

[1] Geuther and Wackenroder, *Zeitsch. Chem.* 1867, 705.
[2] Haushofer, *Zeitsch. Kryst.* i. 619.
[3] Henry, *Ber. Deutsch. Chem. Ges.* v. 949.

The ketonic acids obtained by this reaction are not known in the free state, though their ethereal salts have been prepared.

*Ethyl Propionyl-propionate,* $CH_3.CH_2.CO.CH_2.CH_2.CO_2C_2H_5$, is formed by the action of sodium on ethyl propionate, the product being treated with acetic acid. It is a pleasantly smelling liquid boiling at 199°, having a specific gravity at 0° of 0·9948, and not yielding any coloration of ferric chloride.[1]

The following compounds have also been obtained by the aceto-acetic acid reaction:

| | B.P. | Sp. Gr. | at |
|---|---|---|---|
| [2] Ethyldimethyl-acetacetate, $CH_3.CO.C(CH_3)_2CO_2.C_2H_5$ | 184° | 0·9913 | 16° |
| [3] Methylethyl-acetacetate, $CH_3.CO.CH(C_2H_5)CO_2.CH_3$ | 189°·7 | 0·995 | 14° |
| [4] Ethylethyl-acetacetate, $CH_3.CO.CH(C_2H_5)CO_2.C_2H_5$ | 198° | 0·998 | 12 |
| [5] Amylethyl-acetacetate, $CH_3.CO.CH(C_2H_5).CO.C_5H_{11}$ | 235° | 0·937 | 26° |

The ethyl salt of ethyl-acetacetic acid is converted by the action of sodium amalgam and water into *Ethyl-β-oxybutyric acid,* $CH_3.CH(OH).CH(C_2H_5).CO_2H$. This forms a syrup, and on standing in a vacuum is converted into an anhydrido-compound.[6]

## ACIDS HAVING THE FORMULA $C_6H_{10}O_4$.

644 *Adipic Acid,* $C_4H_8(CO_2H)_2$. Laurent, in 1837, pointed out that when oleic acid, $C_{18}H_{34}O_2$, is oxidized, a series of dibasic acids are formed, to which he gave the names lipinic acid, $C_5H_8O_4$; adipic acid, $C_6H_{10}O_4$; pimelic acid, $C_7H_{12}O_4$; suberic acid, $C_8H_{14}O_4$; and azelaic acid, $C_9H_{16}O_4$.[7] Bromeis carried on similar experiments with stearic acid and oleic acid, and obtained succinic acid in addition to the above.[8] Further

[1] Hellon and Oppenheim, *Ber. Deutsch. Chem. Ges.* x. 699.
[2] Frankland and Duppa, *Phil. Trans.* 1866, 37.
[3] Brandes, *Zeitsch. Chem.* 1866, 457.
[4] Geuther, *Jahresb.* 1863, 324; Frankland and Duppa, *loc. cit.*; Wislicenus, *Ann. Chem. Pharm.* clxxxvi. 187; Miller, *ib.* cc. 281.
[5] Conrad, *ib.* clxxxvi. 228.
[6] Waldschmidt, *ib.* clxxxviii. 240.
[7] *Ann. Chim. Phys.* lxvi. 154.
[8] *Ann. Chem. Pharm.* xxxv. 86.

research showed that spermaceti,[1] tallow,[2] and wax,[3] yield chiefly adipic acid, and lastly Wurtz, by oxidizing the solid fatty acids of cocoa-nut oil obtained not only the products observed by Laurent and Bromeis, but also oxalic acid. Still the existence of several of these acids remained doubtful until the investigations of Arppe. This chemist discovered methods by which these acids can be completely separated one from the other, as was not formerly the case. Arppe showed that lipinic and pimelic acid do not occur in the products of the oxidation of fats, but that the substances supposed to be these acids are really mixtures. He proved, moreover, that the pure acids all crystallize perfectly well, these having previously only been obtained in crystalline crusts or warty concretions.[4] According to the former methods for preparing adipic acid, the higher homologues which are more difficultly soluble in water are separated by crystallization, and the adipic acid obtained by concentrating the mother-liquor, and further purifying by recrystallization. According to Arppe adipic acid is formed, together with suberic acid and azelaic acid, from sebacic acid $C_{10}H_{18}O_4$, which itself is first produced by the oxidation of the fatty acids as well as by other reactions. This body serves, therefore, as the best means of obtaining adipic acid, succinic acid being the only other body which is formed at the same time. For this preparation, sebacic acid is boiled with nitric acid until it has been converted into a mixture of the two acids, which are soluble in water. The nitric acid is then evaporated off and the adipic acid crystallized out from water. It is then fused, the solidified mass powdered and treated with ether which dissolves the acid, whilst a little succinic acid remains behind.

Adipic acid was prepared synthetically by Wislicenus by treating $\beta$-iodopropionic acid, $CH_2I.CH_2.CO_2H$, with finely divided silver. This shows that it is the normal compound.[5] It dissolves in about 18 parts of cold water, and much more readily in hot water, alcohol, and ether, and crystallizes in laminæ or flattened needles, melting at 148°—149°.

The salts of adipic acid have been investigated by Arppe. Of

[1] *Sillim. Journ.* xliii. 301; Smith, *ib.* xlii. 252.
[2] Malaguti, *Ann. Chim. Phys.* [3], xvi. 84.
[3] Gerhardt, *Rev. Scient.* xiii. 302.
[4] *Jahresb.* 1864. 377.
[5] *Ann. Chem. Pharm.* cxlix. 221.

these *ammonium adipate* is the most characteristic, depositing in monoclinic crystals resembling those of augite.

*Ethyl Adipate*, $C_4H_8(CO_2.C_2H_5)_2$, was first observed by Malaguti in the products of the action of hydrochloric acid on an alcoholic solution of impure adipic acid. It is described as an oily liquid having a strong smell of apples. According to Arppe it boils without decomposition at 245°.

645 *Substitution-products of Adipic Acid.* Mono- and dibrom-adipic acids are obtained by the action of bromine. The first when heated with alkalis yields *adipomalic acid*, $C_4H_7(OH)(CO_2H)_2$, forming a syrup which gradually crystallizes. Its lead salt is a precipitate which, like the corresponding malate, melts under boiling water. The dibromadipic acid yields, on heating with water to 150°, adipotartaric acid, $C_4H_6(OH)_2(CO_2H)_2$, a body crystallizing from boiling water in monoclinic tables, and forming a difficultly soluble acid potassium salt.[1]

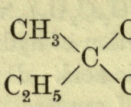
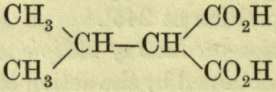
The following acids isomeric with adipic acid have been obtained from ethyl acetacetate:

| | | | M.P. |
|---|---|---|---|
| [2] Ethyl succinic acid, | $C_2H_5.CH.CO_2H$ <br> $CH_2.CO_2H$ | Fine prisms. | 98° |
| [3] *a*-Dimethyl-succinic acid, | $(CH_3)_2C.CO_2H$ <br> $CH_2.CO_2H$ | Needles. | 74° |
| [4] *β*-Dimethyl-succinic acid, | $CH_3.CH.CO_2H$ <br> $CH_3.CH.CO_2H$ | Crystals. | 165-167° |
| [5] *a*-Methyl-glutaric acid, | $CH_3.CH.CO_2H$ <br> $CH_2.CH_2.CO_2H.$ | Crystals. | 76° |

*β*-methyl-succinic acid is also formed when *a*-brompropionic acid is heated with finely divided silver.[6]

[1] Gal and Gay-Lussac, *Compt. Rend.* lxx. 1175.
[2] Huggenberg, *Ann. Chem. Pharm.* cxcii. 148.
[3] Tate, *Inaugural Dis.* Würzburg, 1880.
[4] Hardtmuth, *Ann. Chem. Pharm.* cxcii. 143.
[5] Wislicenus and Limpricht, *ib.* cxcii. 134.
[6] Wislicenus, *Ber. Deutsch. Chem. Ges.* ii. 720.

The following acids have been obtained from ethyl malonate :

| | | M.P. |
|---|---|---|
| [1] Methyl-ethyl-malonic acid,  | Prisms. | 118° |
| [2] Isopropyl-malonic acid,  | Prisms. | 87° |
| [3] Propyl-malonic acid, $C_3H_7.CH\begin{matrix}CO_2H\\CO_2H\end{matrix}$ | Tables | 96° |

*Dimethyl-dioxysuccinic Acid*, or *Dimethyl-tartaric Acid*,

$$\begin{matrix}CH_3.C(OH).CO_2H\\|\\CH_3.C(OH).CO_2H,\end{matrix}$$

is formed together with lactic acid by the action of zinc on an alcoholic solution of pyroracemic acid. The acid obtained from the insoluble zinc salt remains as a syrup on evaporating its solution. The characteristic calcium salt is a crystalline almost insoluble precipitate.[4]

[1] Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 146.
[2] *Ib.* 144. [3] *Loc. cit.*
[4] Böttinger, *Ann. Chem. Pharm.* clxxxviii. 315.

## THE HEPTYLENE COMPOUNDS.

646 *Normal Heptylene*, $C_7H_{14}$, can exist in three isomeric forms. Of these Limpricht has obtained *pentyl-ethylene*, $C_5H_{11}.CH{=}CH_2$, from œnanthol by treating it with phosphorus pentachloride and decomposing with sodium the œnanthidene dichloride, $C_7H_{14}Cl_2$, thus obtained, which is a liquid boiling at 191°.

Pentyl ethylene is a liquid possessing an alliaceous smell and boiling at 95°. The heptylene obtained from *Pinus sabiniana* is a similar liquid boiling at 98°. On oxidation it is split up into acetic and pentoic acids, and it is consequently *methyl-butyl-ethylene*, $CH_3.CH{=}CH.C_4H_9$ (Schorlemmer and Thorpe).

*Isoheptylene*, $(CH_3)_2C_5H_8$. If the mixture of primary and secondary heptyl chloride obtained by the action of chlorine on isoheptane be boiled with potassium acetate and glacial acetic acid, an heptylene is obtained in addition to the corresponding acetates. This boils at 91°, and combines almost entirely with hydrochloric acid in the cold,[1] and is probably identical with the heptylene obtained from methyl-amyl-carbinol by decomposing its iodide with alcoholic potash.[2]

*Diethyl-methyl-ethylene*, $C_2H_5.CH{=}C(CH_3)C_2H_5$, is a liquid boiling between 90° and 95°, obtained from methyl-ethyl-propyl-carbinol, whilst methyl-ethyl-isopropyl-carbinol yields *ethyl-trimethyl-ethylene* $(CH_3)_2.C{=}C(CH_3)C_2H_5$, a body boiling at between 75° and 80°.[3]

*Dimethyl-isopropyl-ethylene*, $(CH_3)_2C.{=}CH.CH(CH_3)_2$, was obtained first by Markownikow by heating oxyisocaproic acid, $(C_3H_7)_2(COH)CO_2H$, with water and a little sulphuric acid to 180°.[4] Pawlow obtained it from dimethyl-isobutyl-carbinol.[5] It boils at 83°—84°, has a specific gravity at 0° of 0·7144, and

[1] Grimshaw, *Chem. Soc. Journ.* [2], xi. 209; Schorlemmer, *ib.* 323.
[2] Rohn, cxc. 314.
[3] Pawlow, *Ber. Deutsch. Chem. Ges.* ix. 1311.
[4] *Zeitsch. Chem.* 1870, 518; 1871, 268.
[5] *Ann. Chem. Pharm.* clxxvii. 194.

combines readily with hydriodic acid to form the iodide of the tertiary alcohol.

*Trimethylcarbyl-methyl-ethylene*, $(CH_3)C_3.C(CH_3) \equiv CH_2$, was obtained by Butlerow by heating pentamethyl-ethyl iodide with alcoholic potash. It boils at 75°—80°, smells like camphor and oil of turpentine, and combines readily again with hydriodic acid to form the tertiary iodide. When left in contact with water to which a small quantity of alcohol and nitric acid has been added, it forms pentamethyl-ethol (Part I., p. 645).[1]

## OXYACIDS HAVING THE FORMULA $C_7H_{14}O_3$.

| | | M.P. |
|---|---|---|
| [2] Oxycenanthylic acid, $C_5H_{11}.CH(OH)CO_2H$ | Prisms. | 65° |
| [3] Amyl-hydroxalic acid, $(CH_3)_2C_3H_5.CH(OH)CO_2H$ | Scales. | 60°·5 |
| [4] Methyl-ethyl-oxybutyric acid, $CH_3.CH(OH)C(CH)(C_2H_3)—CO_2H$ | Syrup. | — |
| [5] Methyl-propyl-ethylene-lactic acid, $(CH_3)(C_3H_7)C(OH).CH_2.CO_2H$ | Syrup. | — |
| [6] Diethyl-ethylene-lactic acid, $(C_2H_5)_2C(OH)CH_2.CO_2H$ | Needles. | 71-73° |

## KETONIC ACID, $C_7H_{12}O_3$.

| | B.P. |
|---|---|
| [7] Ethyl methyl-ethyl-acetacetate, $CH_3.CO.C(CH_3)(C_2H_5)—CO_2.C_2H_5$ | 198° |
| [8] Ethyl isopropyl-acetacetate, $CH_3CO.CH(CH(CH_3)_2)CO_2.C_2H_5$ | 201° |

647 The first of these compounds yields a violet colour with ferric chloride, and on heating with sodium ethylate free from alcohol, forms together with ethyl acetate the ethyl salt of methyl-ethyl-acetic acid. The second salt yields a pale reddish violet colour with ferric chloride.[9]

[1] Butlerow, *Ber. Deutsch. Chem. Ges.* viii. 166.
[2] Helms, *ib.* viii. 1169 ; Ley, *ib.* x. 231.
[3] Frankland and Duppa, *Proc. Roy. Soc.* xiv. 191.
[4] Saur, *Ann. Chem. Pharm.* clxxxviii. 257.
[5] Zemlianicin, *Ber. Deutsch. Chem. Ges.* xii. 2375. [6] Schirokow, *ib.*
[7] Saur, *loc. cit.* [8] Frankland and Duppa, *Journ. Chem. Soc.* [2], v. 102.
[9] Demarcay, *Bull. Soc. Chim.* xxvii. 224.

## DIBASIC ACIDS, $C_7H_{12}O_4$.

648 *Pimelic Acid*, $C_5H_{10}(CO_2H)_2$. It has already been stated that Laurent believed that he found an acid of this composition amongst the oxidation products of oleic acid, whilst other chemists obtained the same acid by the oxidation of other fatty acids or fats, and also that Arppe showed that the substance thus obtained is a mixture of adipic and suberic acids. An acid having the above composition is, however, obtained by fusing camphoric acid, $C_8H_{14}(CO_2H)_2$, with caustic potash, and the name of pimelic acid, which was suggested by Laurent, has been retained for this body.[1] It forms crystalline crusts or triclinic crystals which melt at 114°, and are very soluble in water, alcohol, and ether. The calcium salt is a characteristic one. It is difficultly soluble in cold, and even less soluble in boiling water, and hence, on warming the cold saturated solution, the salt precipitates as a crystalline powder. On distillation, the acid decomposes into water and the anhydride $C_7H_{10}O_3$, a thick oily liquid which boils at 245°-250°. Pimelic acid is probably *isopropylsuccinic acid* $(CH_3)_2.CH.CH(CO_2H).CH_2.CO_2H$.[2]

*α-Pimelic Acid* is formed by the oxidation of suberone, $C_7H_{12}O$, with nitric acid[3] as well as by heating furonic acid, $C_7H_8O_5$, with hydriodic acid and amorphous phosphorus.[4] It crystallizes from hot water in large thin rhombic tables, and from benzene in fine long needles, which melt at 100° and volatilize without decomposition. Its calcium salt is also less soluble in hot than in cold water, and separates on heating the cold saturated solution as a granular crystalline precipitate.

*Isopimelic Acid* was obtained from common amylene, which as has been stated is a mixture of isomeric olefines, by combining it with bromine and heating the product with potassium cyanide and alcohol. It is easily soluble in water, alcohol, and ether, crystallizes in rhombic needles concentrically grouped, and melts at 104°. The difficultly soluble calcium salt is also characteristic, as its solubility increases to begin with, on rise of temperature, and then gradually diminishes.[5]

[1] Hlasiwetz and Grabowsky, *Ann. Chem. Pharm.* cxlv. 207 ; Kachler, *ib.* clxix. 168.
[2] Waltz, *Ann. Chem. Pharm.* ccxiv. 58.
[3] Dale and Schorlemmer, *Chem. Soc. Trans.* 1879, 683.
[4] Baeyer, *Ber. Deutsch. Chem. Ges.* x. 1358.
[5] Bauer and Schuler, *Wien. Akad. Ber.* lxxvii. 289.

*Diethyl-malonic Acid*, $(C_2H_5)_2C(CO_2H)_2$. The ethyl salt of this acid is formed when one molecule of ethyl malonate is treated with an alcoholic solution of two molecules of sodium malonate and two molecules of ethyl iodide. It is an oily liquid having a faint but pleasant smell, and boiling at 223°. The acid obtained from this is easily soluble in water, alcohol, and ether, and crystallizes in prisms which melt at 121°. When it is neutralized with ammonia and calcium chloride added, a crystalline precipitate is formed only when the solution is very concentrated, the separation of which is accelerated by warmth.[1]

*Isobutyl-malonic Acid*, $(CH_3)_2C_2H_3.CH(CO_2H)_2$. By the action of isobutyl iodide on ethyl sod-malonate, ethyl isobutyl-malonate is obtained. This liquid boils at 225°. The acid prepared from this is crystalline, easily soluble in water, alcohol, and ether, and melts at 107°. The solution neutralized with ammonia yields a crystalline precipitate with calcium chloride.

By the action of chlorine on the ethyl salt a monochlorinated ethereal salt, $(CH_3)_2C_2H_3.CCl(CO_2.C_2H_5)_2$, is obtained, boiling between 245° and 247°. When treated with alcoholic caustic potash *isobutyloxymalonic acid*, or *isobutyl-tartronic acid*, $(CH_3)_2C_2H_3.C(OH)(CO_2H)_2$, is obtained, a crystalline body which is highly hygroscopic and deliquescent, and melts at 110°—114°. When heated to 180° it decomposes into carbon dioxide and oxyisocaproic acid.[2]

*Isopropylsuccinic acid*, $CO_2H.CH[(CH_3)_2CH]CH_2.CO_2H$, is prepared by the acetacetic reaction; it is readily soluble in water, crystallizes well, and melts at 114°.[3]

[1] Conrad, *Ann. Chem. Pharm.* cciv. 138.
[2] Guthzeit, *Ann. Chem. Pharm.* ccix. 232.
[3] Roser, *Ber. Deutsch. Chem. Ges.* xv. 295.

## THE OCTYLENE COMPOUNDS.

649 *Normal Octylene* or *Caprylene*, $C_8H_{16}$, is formed by the distillation of secondary octyl alcohol with anhydrous zinc chloride. It is a colourless rather strongly-smelling liquid, boiling at 125°, and having at 17° a specific gravity of 0·723.[1] Möslinger obtained an octylene boiling at 122°-123°, and having a specific gravity at 17° of 0·7127 by heating primary octyl alcohol with iodine and amorphous phosphorus.[2] This evidently is *hexyl-ethylene*, $C_6H_{13}.CH = CH_2$. and is probably identical with that obtained from secondary octyl alcohol or its iodide, which, however, may also be methyl-pentyl-ethylene, $C_5H_{11}.CH = CH.CH_3$.

*Octylene Glycol*, $C_8H_{16}(OH)_2$, is obtained from octylene bromide, a heavy liquid, decomposing on distillation, and being converted by the action of silver acetate and glacial acetic acid into *octylene diacetate*, a liquid boiling at 245°—250°. By heating with caustic potash the glycol is obtained as an oily liquid having a burning taste, boiling at 235°—240°, and having at 0° a specific gravity of 0·932.[3]

When this compound is treated with hydrochloric acid, or when octylene is brought in contact with dilute hypochlorous acid, *octylene chlorhydrate*, $C_8H_{16}Cl(OH)$, is formed. This is a mobile liquid having a camphor-like smell and a burning taste. It is not volatile without decomposition, is insoluble in water, and at 0° has a specific gravity of 1·003.

*Octylene Oxide*, $C_8H_{16}O$, is obtained by the action of caustic potash on the chlorhydrin. It is a mobile liquid having a pleasant aromatic smell, boiling at 145° and having at 15° a specific gravity of 0·831.[4]

*Octylene Chloride*, $C_8H_{16}Cl_2$, is an oily liquid, boiling at 197°—200°.[5]

[1] Bouis, *ib.* xcii. 396. [2] *Ann. Chem. Pharm.* clxxxv. 52.
[3] de Clermont, *Ann. Chem. Pharm.* Suppl. iii. 254.
[4] de Clermont, *Ann. Chem. Pharm.* clvi. 122. [5] Dachauer, *ib.* cvi. 271.

*Nitro-octylene*, $C_8H_{15}NO_2$, is formed together with dinitro-octylene by the action of nitric acid on octylene. It is a yellow oily liquid, lighter than water, and when heated to the boiling point it has an unpleasant, powerful, pungent smell. It is coloured red by caustic potash, and dissolves in the concentrated ley.

*Dinitro-octylene*, $C_8H_{14}(NO_2)_2$, is obtained by the action of a mixture of sulphuric and nitric acids on the foregoing compound. It is a heavy oily liquid dissolving slightly in water, imparting to it a yellow colour and a very powerful pungent smell. When heated the boiling-point rises from 100° to 200°, and if the lamp be then removed the temperature rises to 212°, with evolution of red vapours, whilst pure nitro-octylene distils over, a black residue soluble in potash remaining in the retort.[1] Hydriodic acid decomposes it below 100°, with formation of octylene and ammonia, and of a heavy oil which is probably octyl iodide.[2]

*Di-isobutylene* or *Dimethyl-pseudobutyl-ethylene*, $(CH_3)_2C{=}CH.C(CH_3)_3$. In order to prepare this compound one volume of liquid isobutylene is brought in contact with two volumes of a mixture of equal weights of water and sulphuric acid in closed tubes. After standing one or two days the olefine is dissolved, and the mixture is then heated for another day to 100°. The following equation represents the formation of this compound:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CH_2 + HO.C\!\!<\!\!\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CH.C\!\!<\!\!\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix} + H_2O.$$

It is, therefore, also formed when one part of trimethyl-carbinol and two volumes of the dilute acid are heated to 100°,[3] as well as when isobutylene is heated with tertiary butyl iodide and lime.[4]

Di-isobutylene is a liquid which smells like petroleum, boils at 102°·5, and at 0° has a specific gravity of 0·734. It easily combines with hydrochloric and hydriodic acids with formation of the haloid ethereal salts of isodibutol (Part I., p. 655). It is oxidized by chromic acid solution in the cold, with formation of acetone and trimethyl-acetic acid, acetic acid being produced at the same time, as well as the ketone $(CH_3)_3C.CH_2.CO.CH_3$, and an octoic acid, $C_8H_{16}O_2$. The formation of this latter

[1] Bouis, *Ann. Chim. Phys.* [3], xliv. 118.
[2] Mills, *Jahresb.* 1864, 517.
[3] Butlerow, *Ann. Chem. Pharm.* clxxxix. 44.
[4] Julie Lermontoff, *Ann. Chem. Pharm.* cxcvi. 116.

compound is explained by Butlerow by the assumption that during the oxidation a part of the di-isobutylene combines with water to form di-isobutol, and that this again decomposes into water and an octylene having the following constitution:

$$(CH_3)_3C.CH_2C\begin{cases}CH_3\\CH_2.\end{cases}$$

When this re-combines with water a primary alcohol is formed, and this by oxidation yields the octoic acid, which is an oily liquid similar to trimethyl-acetic acid, though possessing a less powerful smell and decomposing somewhat on distillation.

When on the other hand, di-isobutylene is oxidized with potassium permanganate, it yields, together with trimethyl-acetic acid, the oxyoctoic acid shortly to be described, and also *oxyoctenol*, $C_8H_{16}O_2$. This crystallizes in needles, melts at 49°.5, boils at 178°—178°.5, and has a camphor-like smell. It contains an hydroxyl group and has the constitution $(CH_3)_3C.CO.C(OH)(CH_3)_2$.[1]

*Di-isopropyl-ethylene*, $(CH_3)_2CH.CH{=}CH.CH(CH_3)_2$. When the mixture of primary and secondary chlorides, got by acting upon di-isobutyl with chlorine, is heated with potassium acetate and acetic acid, an octylene which probably possesses the above constitution is obtained, together with the corresponding acetates (Part I., p. 654). This boils at 122°, and at 16° has a specific gravity of 0·7526.[2]

*Methyl-ethyl-pinacone* or *Diethyl-dimethyl-ethylene Glycol*, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C(OH).C(OH)<\!\!\begin{matrix}CH_3\\C_2H_5\end{matrix}$, is formed, together with methyl-ethyl-carbinol, when methyl-ethyl ketone is brought in contact with a concentrated solution of carbonate of potash, and sodium gradually added. It is a white crystalline mass which melts at 28° and boils at 200°—205°. When boiled with dilute sulphuric acid it is converted into the corresponding pinacoline (Part I., p. 663), and this on oxidation decomposes into acetic acid and ethyl-dimethyl-acetic acid. Hence it possesses the following constitution:

$$C_2H_5.CO.C\begin{cases}CH_3\\-C_2H_5.\\CH_3\end{cases}$$

It is a liquid possessing strong camphor-like smell, and boiling at 145°—150°.[3]

[1] Butlerow, *Ber. Deutsch. Chem. Ges.* xv. 1575.
[2] W. Carleton-Williams, *Journ. Chem. Soc.* 1877, i. 541.
[3] Lawrinowitsch, *Ann. Chem. Pharm.* clxxxv. 124.

## OXYACIDS, $C_8H_{16}O_3$.

| | | M.P. |
|---|---|---|
| [1] Oxycaprolc acid, $C_6H_{13}.CH(OH).CO_2H$ | Tables. | 69°·5 |
| Oxyoctoic acid $(CH_3)_3C.CH_2.C(OH)CH_3.CO_2H$. | Prisms. | 117° |
| [2] Dipropyl-oxalic acid, $(C_3H_7)_2C(OH).CO_2H$ | Prisms. | 80°-81° |
| [3] Di-isopropyl-oxalic acid, $[(CH_3)_2CH]_2.C(OH).CO_2H$ | Needles. | 110°-111° |
| [4] Diethyl-oxybutyric acid, $CH_3.CH(OH).C(C_2H_5)_2.CO_2H$ | Syrup. | — |

## KETONIC ACIDS, $C_8H_{14}O_3$.

| | B.P. |
|---|---|
| [5] Ethyl diethyl-acetacetate, $CH_3.CO.C(C_2H_5)_2.CO_2C_2H_5$ | 218° |
| [6] Ethyl isobutyl-acetacetate, $CH_3.CO.CH\langle^{CH_2.CH(CH_3)_2}_{CO_2C_2H_5}$ | 217°-218° |

## DIBASIC ACIDS, $C_8H_{14}O_4$.

650 *Suberic Acid*, $C_6H_{12}(CO_2H)_2$. This acid was first obtained by Brugnatelli, in 1787, by heating cork with nitric acid. According to the then prevailing views, he considered that this acid exists already formed in cork, which he believed to consist of this peculiar acid combined with phlogiston and a small quantity of earth, these being withdrawn from the cork by means of the nitric acid.[7] Brugnatelli also found that paper, when treated with nitric acid, yields suberic acid.[8] It may also be thus obtained from linen rags or from lignine.[9]

The existence of this acid was again verified, in 1797, by Bouillon-Lagrange, who found that it could be sublimed.[10] Many

[1] Erlenmeyer and Sigel, *ib.* clxxvii. 103; Ley, *Ber. Deutsch. Chem. Ges.* xi. 232.
[2] Rafalsky, *Ber. Deutsch. Chem. Ges.* xiv. 2068.
[3] Markownikow, *Zeitsch. Chem.* 1870, 516; 1871, 268.
[4] Schnapp, *Ann. Chem. Pharm.* cci. 65.
[5] Frankland and Duppa, *Proc. Roy. Soc.* xiv. 458; Wislicenus, *Ann. Chem. Pharm.* clxxxvi. 191; Matthey, *Journ. Prakt. Chem.* [2], vi 160.
[6] Rohn, *Ann. Chem. Pharm.* cxc. 306.
[7] *Crell's Ann.* 1787, 145.
[8] Gehlen, *Ann.* i. 340.
[9] Berzelius, *Lehrb.* iii. Aufl. 8, 47.
[10] *Ann. Chim.* xxiii. 42.

other chemists occupied themselves with the examination of this acid;[1] amongst others, Laurent found that it can be obtained by oxidizing oleic acid with nitric acid. It is also produced by the action of nitric acid on stearic acid,[2] castor oil,[3] linseed oil,[4] and other fats.

Suberic acid was first prepared in the pure state by Arppe, who showed that the compound described under this name always contained azelaic acid, and that this cannot be removed by crystallization from water but easily by treatment with ether.[5] It is to be remarked, however, that Laurent used ether for the separation of the two acids, and he states that much of the suberic acid dissolves; but, as he probably did not repeat the operation, he did not obtain a pure suberic acid. Spiegel then showed that on oxidizing cork, oxalic acid and other acids are formed as well as azelaic acid.[6]

In order to prepare suberic acid, palm oil[7] or castor oil may be employed. In the latter case the oil is allowed to run into boiling nitric acid of specific gravity 1·25 until no further red vapours are evolved;[8] the mass is then distilled with frequent addition of water in order to remove the oenanthylic acid, and the hot liquid then separated from the nitrated oil which occurs with it. On cooling, a mixture of suberic and azelaic acids separates out, and this is recrystallized frequently from hot water and then treated in a Mohr's extraction apparatus with ether until the residue crystallizes well from water. From 100 parts of castor oil, 4 parts of suberic acid and 3·3 parts of azelaic acid are obtained.[9]

When fats are distilled with superheated steam, paraffins and fatty acids are formed, and, together with these, suberic acid and its homologue azelaic acid, $C_9H_{16}O_4$.[10]

Suberic acid dissolves at 15°·5 in 700 parts of water, and is much more easily soluble in boiling water, crystallizing, on cooling, in needles often an inch long or in irregular tables which melt at 140°. In presence of azelaic acid it separates in grains

[1] H. Brandes, *Ann. Pharm.* ix, 295; Chevreul, *Ann. Chim.* lxii. 323; xcvi. 182; Berzelius, *loc. cit.*
[2] Bromeis, *Ann. Chem. Pharm.* xxxv. 89.
[3] Tilly, *Chem. Soc. Mem.* i. 1.
[4] Sacc, *Ann. Chem. Pharm.* li. 222.
[5] *Ib.* cxx. 288; cxxiv. 89.
[6] *Ann. Chem. Pharm.* cxcix. 144.
[7] Gantter and Hell, *Ber. Deutsch. Chem. Ges.* xiii. 1165.
[8] Grote, *Ann. Chem. Pharm.* cxxx. 208; Spiegel, *loc. cit.*
[9] Dale, *Journ. Chem. Soc.* [2], ii. 258.
[10] Cahours and Demarçay, *Compt. Rend.* xciv. 610.

or warty concretions which, according to the quantity of admixture, melt at 120°—130°. When more strongly heated it evolves pungent vapours and sublimes in needles. It boils at about 300° without decomposition. Heated with caustic baryta it decomposes partly into normal hexane and carbon dioxide whilst another part suffers further decomposition.[1]

The salts of suberic acid have been investigated by Arppe, but especially by Gantter and Hell. The difficultly soluble suberates of calcium, barium, and several other metals are somewhat more soluble in cold than in hot water.

*Ethyl Suberate*, $C_6H_{12}(CO_2.C_2H_5)_2$, is obtained by heating suberic acid with alcohol and sulphuric acid. It is a pleasantly smelling liquid which boils at 280°—282° with slight decomposition (Gantter and Hell).

*Suberaldehyde*, $C_8H_{14}O_3$, is formed together with suberic acid and palmitic acid, $C_{16}H_{28}O_4$, when palmitoleic acid, $C_{16}H_{28}O_2$, is oxidized with fuming nitric acid. It is a bright yellow oily liquid boiling at 202°, and is converted by bromine and water into suberic acid.[2]

*Oxysuberic Acids.* When suberic acid is heated with a molecule of bromine, monobromsuberic acid is formed, and this when treated with caustic potash yields an amorphous *suberomaleic acid*, $C_8H_{11}(OH)(CO_2H)_2$, the salts of which crystallize badly. If the double quantity of bromine be employed, dibromsuberic acid is obtained, and this yields with caustic potash *suberotartaric acid*, $C_8H_{10}(OH)_2(CO_2H)_2$, which is also an amorphous substance.[3]

651 *Suberone*, $C_7H_{12}O$. By distilling suberic acid with lime Boussingault obtained a liquid boiling at 186°, whose analysis gave the formula $C_8H_{14}O$, and its vapour a density of 4·392. He called this substance suberyl hydride as it yields suberic acid on oxidation.[4] Tilley repeated these experiments, and found that the crude product when distilled yielded a volatile liquid which he considered to be benzene, whilst at 176° Boussingault's compound came over, leaving behind a black tarry mass. On oxidation he obtained together with suberic acid a considerable quantity of another acid crystallizing in needles, from which he concluded that the so-called suberyl hydride, to which he gave the same formula, is not the radical of suberic acid.[5]

[1] Riche, *Ann. Chem. Pharm.* cxiii. 105 ; Dale, *loc. cit.*
[2] Schröder, *Ann Chem. Pharm.* cxliii. 34.
[3] Gay-Lussac and Gal, *ib.* clv. 251.
[4] *Ann. Chem. Pharm.* xix. 308.
[5] *Chem. Soc. Mem.* i. 1.

Gerhardt then remarked that the formula $C_8H_{14}O$ of suberone as he called it, does not show how it is related to suberic acid, whilst the probable formula $C_7H_{12}O$ does not explain the reformation of suberic acid.[1] Kekulé then assumed that suberone has the formula $C_{14}H_{24}O_2$, and is the ketone of suberic acid, standing to it in the same relation as common acetone does to acetic acid.[2] The formation of two acids is favourable to this view, but on the other hand the vapour density obtained by Boussingault does not correspond to this. The correct formula was determined by Dale and Schorlemmer, who showed that on oxidation no suberic acid, but *a*-pimelic acid is formed, and that the volatile body observed by Tilley is hexane, whilst at the same time other higher boiling products than suberone are obtained.[3]

Suberone is a liquid possessing a peppermint-like smell, boiling at 179°—181°, and having a vapour-density of 3·73.[4] It combines with nascent hydrocyanic acid forming the cyanhydrine or nitril $C_7H_{12}(OH)CN$, a colourless liquid which is decomposed by concentrated hydrochloric acid, with separation of sal-ammoniac, into *oxysuberancarboxylic acid*, $C_7H_{12}(OH).CO_2H$. This crystallizes from water in glistening small tables an inch in length which contain half a molecule of water of crystallization, which they lose at 60°. It crystallizes from hot benzene in anhydrous glistening needles melting at 79°—80° It possesses at first a sweet and then an astringent taste like alum. When heated with hydrochloric acid it is first converted into *chlorsuberancarboxylic acid*, $C_7H_{12}Cl.CO_2H$, a thick liquid attacking the skin, and being converted by alcoholic potash into *suberancarboxylic acid*, $C_7H_{11}.CO_2H$, a body slightly soluble in water, and crystallizing from dilute alcohol in glistening scales melting at 53°—54°. By the action of sodium and water it is converted into *suberancarboxylic acid*, $C_7H_{13}.CO_2H$, a liquid having a fatty acid odour, and volatilizing in a current of steam. When oxidized with nitric acid, a crystalline dibasic acid is obtained having either the formula $C_8H_{12}O_4$, or that of $C_8H_{14}O_4$. The more complete investigation of this will probably explain the constitution of suberone.[5] There is, however, no doubt that suberone is a peculiar ketone in which the carboxyl is not placed between two monad alcohol radicals, but is combined to a diad hexylene.

[1] *Traité Chem. Org.* ii. 732.
[2] *Lehrb.* ii. 41.
[3] *Chem. Soc. Journ.* [2], xii. 935.
[4] Dale and Schorlemmer, *ib.* 1879, i. 686.
[5] Spiegel, *Ann. Chem. Pharm.* ccxi. 117

It is a singular fact that azelaic acid and sebacic acid, the two next highest homologues to suberic acid, do not yield any homologues of suberone on heating with lime, but give a very complicated mixture of different compounds.[1] Succinic acid behaves in a similar way. The calcium salt of this body when submitted to dry distillation was formerly thought to yield a succinone boiling at 120°,[2] but recent investigations have, however, shown that this is a mixture.[3]

*Isosuberic Acid.* When ethyl monobrombutyrate is heated with finely divided silver a singularly smelling liquid boiling at 245°—247°, is formed together with other compounds. This body has the composition of ethyl suberate. It is a mixture of the ethereal salts of two suberic acids, of which one is difficultly soluble in water and crystallizes in feathery grouped needles, melting at 184—185°, whilst the more easily soluble acid forms large crystals which melt at 127°.[4]

Two isomeric acids are obtained in the same way from ethyl bromisobutyrate, of which the readily soluble one crystallizes similarly to succinic acid and melts at 95°, whilst the difficultly soluble one does not melt till 146°·5.[5]

[1] Dale and Schorlemmer, *Journ. Chem. Soc.* 1879, i. 687.
[2] D'Arcet, *Ann Chim. Phys.* [3], ix. 206.
[3] Funaro, *Ber. Deutsch. Chem. Ges.* xiv. 2240.
[4] Hell and Mühlhauser, *ib.* xiii. 479.
[5] Hell and Wittekind, *ib.* vii. 319; Hell, *ib.* x. 2229.

## OLEFINES CONTAINING MORE THAN EIGHT ATOMS OF CARBON.

652 Of these series only a few members are as yet known, and of these only those which have been more exactly described will be here mentioned.

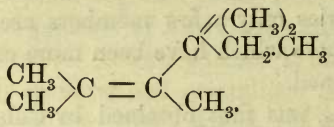
*Diamylene*, $C_{10}H_{20}$, was first obtained by Cahours by the repeated distillation of amyl alcohol over phosphorus pentoxide, and described as *amylene*.[1] Balard then obtained it, together with common amylene, by heating amyl alcohol with zinc chloride, and termed it *paramylene*.[2] Bauer found that it is also easily formed, together with higher polymerides, when amylene obtained from fusel oil is heated with zinc chloride to 100°.[3] According to Cahours and Balard this body boils at 160°, and according to Bauer at 165°, but as common amyl alcohol and the amylene obtained from this are mixtures, and as the reaction produced by zinc chloride is a very complicated one, the diamylene obtained in this way is also doubtless a mixture. On the other hand the diamylene obtained by the action of sulphuric acid on trimethyl ethylene is probably a simple product. This boils at 154°—156°, and has a specific gravity at 0° of 0·7845.[4] The diamylene obtained by the action of sulphuric acid on common amylene[5] or on the mixtures of amylenes produced by heating amyl iodide with alcoholic potash, is probably identical with this.[6] In order to prepare it one volume of common amylene is shaken up at 0° with two volumes of sulphuric acid of specific gravity 1·64.[7]

A peculiar weak oily acid having the composition $C_7H_{14}O_2$

[1] *Ann. Chim. Phys.* lxx. 81. [2] *Ib.* [3], xii. 322.
[3] *Jahresb.* 1861, 660.
[4] Wyschnegradsky, *Ber. Deutsch. Chem. Ges.* viii. 434.
[5] Bauer, *Sitzungb. Wien. Akad.* xliv. [2], 87; Berthelot, *Compt. Rend.* lvi. 1242.
[6] Lebedew, *Ber. Deutsch. Chem. Ges.* viii. 767; *Journ. Russ. Chem. Ges.* vii. 246.
[7] Erlenmeyer, *Zeitsch. Chem.* 1865, 362; Schneider, *Ann. Chem. Pharm.* clvii. 207.

is obtained, together with acetic acid and acetone, by oxidizing diamylene with chromic acid solution. To this body Schneider gave the name of *amethenic acid.* A neutral oil is also formed which has the composition $C_{10}H_{20}O$, when amylene dibromide is heated with water and lead oxide,[1] and this by further oxidation is decomposed into carbon dioxide, acetic acid, and amethenic acid.

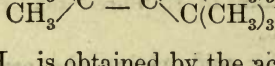
As the formation of diamylene from amylene corresponds to that of di-isobutylene from butylene, it probably possesses, according to Butlerow, the following constitution:



*Hendecatylene,* $C_{11}H_{22}$, is obtained from secondary hendecatyl bromide, and therefore is probably methyl-octyl-ethylene. It is a liquid boiling at 192°—193°.[2]

653 *Tri-isobutylene,* $C_{12}H_{24}$, is obtained when isobutylene is passed into a cold mixture of five parts of sulphuric acid and one part of water,[3] or when di-isobutylene or isobutylene is heated with tertiary butyl iodide and lime to 100°.[4] According to Dobbin it is also formed, together with traces of isobutylene but no di-isobutylene, when the tertiary iodide is brought in contact with zinc oxide at the ordinary temperature.[5] It is a colourless liquid which boils at 177°·5—178°·5, and at 0° has a specific gravity of 0·774. When oxidized with chromic acid solution it yields carbon dioxide, acetone, acetic acid, trimethyl-acetic acid, and methyl-dibutyl-acetic acid, $C_{11}H_{22}O_2$, a body crystallizing from alcohol in glistening scales, melting at 60°—70°, boiling at 266°, and possessing but faintly acid properties.

Tri-isobutylene has most probably the following constitution:



*Di-hexylene,* $C_{12}H_{24}$, is obtained by the action of sulphuric acid on *a*-ethyl-dimethyl-ethylene, and boils at 196°—199°. The isomeric *β*-ethyl-dimethyl-ethylene yields a di-hexylene boiling at 193°—197°.[6]

[1] Eltekow, *Journ. Russ. Chem. Ges.* x. 229.
[2] Giesecke, *Zeitsch. Chem.* 1870, 431. [3] Butlerow, *Jahresb.* 1879, 364.
[4] Julie Lermontow, *Ann. Chem. Pharm.* cxcvi. 116.
[5] *Journ. Chem. Soc.* 1880, I. 236. [6] Jawein, *Liebig's Ann.* cxcv. 261.

In addition to these olefines, others may here be mentioned which are obtained by the distillation of solid paraffin (Part I., p. 137), and by the dry distillation of the lime-soaps of train-oil [1] or occur in Burmah petroleum.[2]

| | From Paraffin. B.P. | Lime Soap. B.P. | Petroleum. B.P. |
|---|---|---|---|
| Nonylene, $C_9H_{18}$ | 145°-148° | 153° | — |
| Decatylene, $C_{10}H_{20}$ | 170°-172° | 174°·6 | 175°·8 |
| Hendecatylene, $C_{11}H_{22}$ | 193°-195° | 195°·4 | 195°·9 |
| Dodecatylene, $C_{12}H_{24}$ | — | 212°·6 | 208°·3-214°·6 |
| Tridecatylene, $C_{13}H_{26}$ | — | — | 232°·7 |

*Triamylene*, $C_{15}H_{30}$, is formed by the action of zinc chloride on amyl alcohol. It is a liquid smelling like turpentine, and boiling at 245°—248°.

In addition to this olefine, tetra-amylene, $C_{20}H_{40}$, is also formed, boiling between 390° and 400°. This body was noticed by Balard and termed by him metamylene.[3]

654 *Cetylene* or *Cetene*, $C_{16}H_{32}$, was obtained by Dumas and Peligot by heating cetyl alcohol with phosphorus pentoxide. It is also formed by boiling cetyl chloride for some time,[4] and is found amongst the products of the dry distillation of spermaceti.[5] It is a liquid boiling at 274°, and having a specific gravity at 15° of 0·7893°.[6] It combines easily with bromine to form *cetylene dibromide*, $C_{16}H_{32}Br_2$, a heavy yellow liquid which decomposes on heating. It also unites with hypochlorous acid to form *cetylene chlorhydrin*, $C_{16}H_{32}Cl(OH)$, an oily liquid boiling at about 300° and being converted by caustic potash into *cetylene oxide*, $C_{16}H_{32}O$, a body crystallizing in small needles melting at 30° and boiling at about 300°.[7]

It has already been mentioned that the so-called oil of wine (*oleum vitrioli dulce*) is a mixture of ethyl sulphate with several olefines (Part I., p. 354). When shaken up with water the sulphate is dissolved, and an oily liquid remains, which on cooling deposits prisms of *etherol*, a body melting at 110°, and boiling at 260°. The liquid separated from this is termed *etherin*, and this does not solidify above —35° and boils at 280°.[8] These two olefines are probably isomeric with cetylene, as is also that

[1] Storer and Warren, *Zeitsch. Chem.* 1868, 229. [2] *Ib.* 231.
[3] *Ann. Chim. Phys.* (3) xii. 326. [4] Tüttschew, *Jahresb.* 1860, 406.
[5] Smith, *Ann. Chem. Pharm.* xlii. 241.
[6] Mendelejeff, *Jahresb.* 1860, 7.
[7] Carius, *Ann. Chem. Pharm.* cxxvi. 201.
[8] Serullas, *Ann. Chim. Phys.* [2], xxxix. 152.

which is obtained together with heptane and other products when azelaic acid is distilled with baryta. This cetylene crystallizes in needles, melts at 41°—42°, and boils at 283°—285°.[1]

*Hexpropylene*, $C_{18}H_{36}$, is formed together with propylene and other polymerides by the action of zinc and acetic acid on propylene bromide. It is a liquid boiling between 390°—400°.[2]

655 *Cerylene* or *Cerotene*, $C_{27}H_{54}$, is formed together with cerotic acid, in the distillation of Chinese wax. It is a paraffin-like mass, melting at 57°—58°. When it is melted in a closed tube bent at right angles, and distilled six or seven times backwards and forwards, it is converted into a mixture of combustible gases and of oily liquids boiling between 75° and 260°.[3] In this respect it resembles solid paraffin.

According to König and Kiesow a solid hydrocarbon is found in hay, and this which melts at 65°—66°, is either an olefine, $C_{27}H_{54}$, or a paraffin.[4]

*Melissylene* or *Melene*, $C_{30}H_{60}$, was obtained by Ettling by distilling beeswax, and was believed by him to be a paraffin.[5] Brodie then obtained it by distilling melissyl alcohol and myricine (Part I., p. 682).[6] It forms colourless crystals which melt at 62°, and are difficultly soluble in cold, but more readily soluble in boiling alcohol.

## OXYACIDS CONTAINING MORE THAN EIGHT ATOMS OF CARBON.

| | | M.P. |
|---|---|---|
| [7] Ethyl-amyl-oxalic acid, $\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\!\!>\!C(OH)CO_2H$ | Crystalline. | — |
| [8] $\beta$-Dipropyl-ethylene-lactic acid, $(C_3H_7)_2.C(OH).CH_2.CO_2H$ | Syrup. | — |
| [9] Diamyl-oxalic acid, $(C_5H_{11})_2.C(OH)CO_2H$ | Silky threads. | 122° |
| [10] Oxymyristic acid, $C_{14}H_{28}O_3$ | Glistening plates. | 57° |
| [11] Oxymargaric acid, $C_{17}H_{34}O_3$ | Plates. | 80° |

[1] Dale and Schorlemmer, *Ann. Chem. Pharm.* cxxxvi. 265.
[2] Prunier, *Compt. Rend.* lxxvi. 98.
[3] Brodie, *Phil. Trans.* 1848 [1], 167.
[4] *Ber. Deutsch. Chem. Ges.* vi. 500.
[5] *Ann. Chem. Pharm.* ii. 255. [6] *Phil. Trans.* 1849, i. 99.
[7] Frankland and Duppa, *Phil. Trans.* 1866, 329.
[8] Schirokow, *Ber. Deutsch. Chem. Ges.* xii. 2375.
[9] Frankland and Duppa, *loc. cit.*
[10] R. Müller, *Ber. Deutsch. Chem. Ges.* xiv. 2476.
[11] Ebert, *Ber. Deutsch. Chem. Ges.* viii. 775.

Oxymyristic acid is found, together with methyl-ethyl-acetic acid in the ethereal oil of the fruit of *Angelia archangelica*.

## KETONIC ACIDS.

| | | B.P. |
|---|---|---|
| Ethyl heptyl-acetacetate, $C_2H_3O.CH(C_7H_{15})CO_2.C_2H_5$ | Primary [1] | 271°-273° |
| | Secondary [2] | 250°-260° |
| [3] Ethyl octyl-acetacetate, $C_2H_3O.CH(C_8H_{17})CO_2.C_2H_5$ | | 280°-282° |
| [4] Ethyl di-isobutyl-acetacetate, $C_2H_3O.C(C_4H_9)_2CO_2.C_2H_5$ | | 250°-253° |
| [5] Ethyl diheptyl-acetacetate, $C_2H_3O.C(C_7H_{15})_2CO_2.C_2H_5$ | | 331°-332° |
| [6] Ethyl dioctyl-acetacetate, $C_2H_3O.C(C_8H_{17})_2.CO_2.C_2H_5$ | | 340°-342° |

## DIBASIC ACIDS.

656 *Azelaic Acid*, $C_7H_{14}(CO_2H)_2$. It has already been stated that Laurent gave this name to an acid which he found amongst the products of oxidation of oleic acid. Buckton then obtained *anchoic acid* by boiling Chinese wax with nitric acid,[7] and Wirz obtained *lepargylic acid* [8] from coco-nut oil. According to Arppe these acids are identical, and he retained for them the original name, and was the first to prepare pure azelaic acid. The particulars of this have already been given under suberic acid, from which acid it is separated by treatment with ether in which it is easily soluble. A mixture of the two acids may also be dissolved in ammonia and fractionally precipitated with calcium chloride, when the calcium salt of azelaic acid is first thrown down.[9]

Azelaic acid crystallizes from water in large thin scales, melting at 106°·5, and dissolving in 900 parts of cold, but in a much smaller quantity of hot water. On heating, the greater portion volatilizes without decomposition and with evolution of pungent vapours, whence its name, from *ἀγχω*, I strangle or suffocate.

[1] Jourdan, *Ann. Chem. Pharm.* cc. 105.
[2] Venable, *Ber. Deutsch. Chem. Ges.* xiii. 1651.
[3] Guthzeit, *Ann. Chem. Pharm.* cciv. 2.
[4] Mixter, *Ber. Deutsch. Chem. Ges.* vii. 500.
[5] Jourdan, *loc. cit.*
[6] Guthzeit, *loc. cit.*
[7] *Journ. Chem. Soc.* x. 166.
[8] *Ann. Chem. Pharm.* civ. 265.
[9] Grote, *Ann. Chem. Pharm.* cxxx. 208; Spiegel, *ib.* cxcix. 145; Gantter and Hell, *Ber. Deutsch. Chem. Ges.* xiv. 560.

Its salts have been investigated by Arppe and by Gantter and Hell.

*α-Azelaic Acid* is formed by heating butyro-furonic acid, $C_9H_{12}O_5$, with hydriodic acid and amorphous phosphorus. It crystallizes from chloroform in small needles which melt at 117°—118°.[1]

657 *Sebacic Acid*, $C_8H_{16}(CO_2H)_2$. The fact that when fats are distilled an acid is obtained was known in the last century. Crell believed it to be a peculiar acid, and termed it fat-acid, and made many experiments upon it in 1778 and 1779, but Thénard in 1801 showed that this volatile acid was acetic acid as Gren had suggested. This same chemist, however, further showed that a much less volatile acid was obtained by distilling lard.[2] This fact was confirmed by V. Rose.[3] It is formed from the oleic acid contained in fats,[4] and can, therefore, be obtained by distilling this acid alone.[5] Berzelius considered this acid to be a benzoic acid, the properties of which were altered by admixture. Its individuality was first established by Dumas and Peligot in 1834.[6]

Sebacic acid is formed together with methyl-hexyl-carbinol when castor-oil soap is heated with caustic alkali,[7] and this reaction serves as the best means of its preparation. For this purpose castor oil is dissolved in an excess of the strongest soda ley, allowed to stand for some time at 40°, the hard cake then separated from the aqueous liquid, and the cake broken up and dried quickly, with stirring, in an iron vessel, and then heated until the smell of capryl alcohol becomes perceptible. It is then poured at once into cold water, and on the addition of hydrochloric the acid separates out.[8] It dissolves in 1000 parts of water at 17°, and in fifty parts at 100°. It is easily soluble, and forms feather-like crystals or thin plates which melt at 127°.

The salts have been investigated by Neison.

By the action of nitric acid on jalapin and some of its derivatives, W. Mayer obtained an acid having the composition of sebacic acid, which, as it melted at 104°, he believed to be distinct from this substance, and termed it ipomic acid.[9] As,

[1] Tönnies, *Ber. Deutsch. Chem. Ges.* xii. 1200.
[2] *Ann. Chim.* xxxix. 193. [3] *Neu. Journ. Chem.* iii. 170.
[4] Gehlen, *Journ. Chem. Phys.* ii. 275.
[5] Redtenbacher, *Ann. Chem. Pharm.* xxxv. 188.
[6] *Ann. Chim. Phys.* lvii. 332. [7] Bouis, *.b.* [3], xliv. 100; xlviii. 99
[8] O. N. Witt, *Ber. Deutsch. Chem. Ges.* vii. 220; see also Neison, *Journ. Chem. Soc.* 1874, 301.
[9] *Ann. Chem. Pharm.* lxxxiii. 145.

however, Neison and Bayne found, this substance is really sebacic acid, Mayer not having properly purified his product.[1]

*Heptyl-malonic Acid*, $(C_7H_{15})CH(CO_2H)_2$, is obtained by the action of secondary heptyl bromide on ethyl sod-malonate. It forms crystals which melt at 97°—98°.[2]

*Brassylic Acid*, $C_9H_{18}(CO_2H)_2$, is formed, together with dioxybehenoleic acid and brassylic anhydride by the action of fuming nitric acid on behenoleic acid, $C_{22}H_{40}O_2$, the chief product being the aldehyde, a light oily liquid which is oxidized to brassylic acid by means of bromine and water. The acid is scarcely soluble in cold, and only slightly soluble in boiling water. It dissolves readily in ether and crystallizes in scales which melt at 108°·5.[3]

*Roccellic Acid*, $C_{15}H_{30}(CO_2H)_2$, was discovered by Heeren in the lichens *Roccella fuciformis* and *Lecanora tartarea*,[4] and further examined by Liebig,[5] Kane,[6] and Schunck.[7] Its exact composition was determined by Hesse.[8] In order to prepare it the lichens are treated with dilute ammonia, the solution precipitated by chloride of calcium, and the washed precipitate decomposed with hydrochloric acid. Roccellic acid is insoluble in boiling water, but dissolves very easily in alcohol and ether, and crystallizes in silver-white rectangular four-sided tables which melt at 130°, and at a higher temperature partially volatilize, another part being converted into the oily anhydride.

*Dioctyl-malonic Acid*, $(C_8H_{17})_2C(CO_2H)_2$, is insoluble in water, and separates out from hot benzene in crystals which melt at 75°.[9]

[1] *Journ. Chem. Soc.* 1874, 729.
[2] Venable, *Ber. Deutsch. Chem. Ges.* xiii. 1651.
[3] Haussknecht, *Ann. Chem. Pharm.* cxliii. 45.
[4] *Schweigg. Journ.* lix. 346.
[5] *Pogg. Ann.* xxi. 31.
[6] *Phil. Trans.* 1840, 299.
[7] *Chem. Soc. Journ.* iii. 153.
[8] *Ann. Chem. Pharm.* cxvii. 332.
[9] Conrad and Bischoff, *ib.* cciv. 163.

## THE URIC ACID GROUP.

658 *Uric Acid*, $C_5H_4N_4O_3$. The attention of the alchemists, and especially of Paracelsus, was naturally directed to the peculiar deposits known as urinary concretions. In comparing, as was his wont, the changes which occur in the animal body with those which take place in ordinary chemical reactions, Paracelsus explained that the deposition of these concretions was similar to that of cream of tartar observed in the manufacture of wine, and hence these bodies were classed together by him under the name of *tartarus*. Van Helmolt held similar views, but he made these deposits the subject of an experimental investigation, and observed that on dry distillation they yielded the volatile alkali, a yellow crystalline mass, some combustible oil, and carbon.[1] Similar experiments were made by other chemists. But the examination of uric acid in the wet way yielded no important results, until Scheele in 1776 discovered uric acid and showed that certain of these concretions dissolve in alkali, and are reprecipitated on the addition of acids. He likewise noticed that they dissolve in nitric acid with evolution of nitrous vapours and fixed air, and that the solution on evaporation leaves a red residue. In one passage Scheele explains that the concretion is an oily salt in which the acid is in excess, and in another he calls it a new acid.[2] About the same time Bergman was occupied in an investigation of a urinary calculus and he also noticed the formation of the red colour produced by the action of nitric acid.[3]

Uric acid was first termed lithic acid, the name which it now bears having been introduced by Pearson in 1797 in the form of uric oxide,[4] whilst Fourcroy, in 1799, designated it as *acid urique*.[5]

[1] Tractate *de Lithiasa*, 1644.
[2] *Opusc.* ii. 73 ; *Crell. N. Entdeck.* iii. 227.
[3] *Opusc.* iv. 387 ; *Crell.* iii. 232.
[4] Scherer, *Journ. Chem.* i. 48.
[5] *Ann. Chem.* xvi. 116 ; xxvii. 225.

Amongst the numerous chemists who have investigated uric acid the names of Liebig and Wöhler deserve the first mention. In their classical research they showed that the acid yields a large number of derivatives, which may be grouped together under alloxan, $C_4H_2N_2O_4$, and parabanic acid, $C_3H_2N_2O_3$.[1] Schlieper then made us acquainted with many other derivatives,[2] but it is to Baeyer's investigation that we are indebted for the first clear insight into the constitution of these somewhat complicated compounds, inasmuch as he showed that most of these derivatives are compound ureas containing acid radicals.[3]

Uric acid is a product of the metabolism of the animal organism. It occurs in human urine, which normally contains about 0·5 grams per diem. It is likewise found in the urine of other mammalia, especially in that of the carnivora, and also in carnivorous and graminivorous birds and reptiles. The excrement of insects and other lower animals also contains uric acid; it is likewise found in the flesh of the alligator, and in the lungs, spleen, liver, and brain of the ox.[4] In gout and other diseases it occurs in the blood as the acid sodium salt,[5] and it is deposited in the joints, as so-called chalk stones, and is also found in various secretions, as in the saliva, perspiration, gastric juice, &c.[6] Urinary concretions, as well as the buff-coloured sediment or muddiness observed in the urine of man and of many animals, usually consists of uric acid or acid ammonium urate, and this re-dissolves when the urine is warmed.

Amido-acids, such as glycocoll, leucine, aspartic acid,[7] as well as urea itself,[8] when brought into the organism of fowls are changed to uric acid found in the urine.

*Preparation.* Uric acid was formerly prepared either from urine, from urinary concretions, or from the excrement of graminivorous birds and serpents.[9] Guano is now best employed for the purpose, and not long ago uric acid was manufactured on a large scale from this source for the preparation of the red

[1] *Ann. Chem. Pharm.* xxvi. 241. [2] *Ib.* lvi. 1.
[3] *Ib.* cxxvii. 1 and 199; cxxx. 129.
[4] On the Occurrence of Uric Acid, see Gmelin's *Handbook*, vol. x. p. 455.
[5] Garrod, *Med. Chir. Trans.* xxxi. 83. *Ib.* xxxvii. 826.
[6] Boucheron, *Compt. Rend.* xciii. 391.
[7] Knieriem, *Ber. Deutsch. Chem. Ges.* x. 1930; Jaffe and Meyer, *ib.*
[8] Braconnot, *Ann. Chim. Phys.* xvii. 392; Prout, *Phil. Trans.* 1818, 420; Bensch, *Ann. Chem. Pharm.* liv. 189; Allen and Bensch, *ib.* lxv. 181; Fritsche, *Journ. Prakt. Chem.* xiv. 245; Arppe, *Ann. Chem. Pharm.* lxxxvii. 237.
[9] Bibra, *Ann. Chem. Pharm.* liii. 111; Bensch, *ib.* lviii. 266; Löwe, *Journ. Prakt. Chem.* xcvi. 408.

colouring-matter murexide, the demand for which has, however, now disappeared, owing to the introduction of aniline red.

In order to prepare uric acid, guano is first moistened with dilute hydrochloric acid, to dissolve the oxalates, carbonates, and phosphates which are present. The residue is then boiled with caustic soda, and the clear solution acidified with hydrochloric acid. If the uric acid which is then precipitated be not colourless, a small quantity of potassium permanganate or potassium bichromate is added to the boiling alkaline solution, and the uric acid then reprecipitated by hydrochloric acid, the precipitate being afterwards repeatedly boiled with strong hydrochloric acid. The crude acid may also be dissolved in concentrated sulphuric acid, and precipitated by the addition of water.[1]

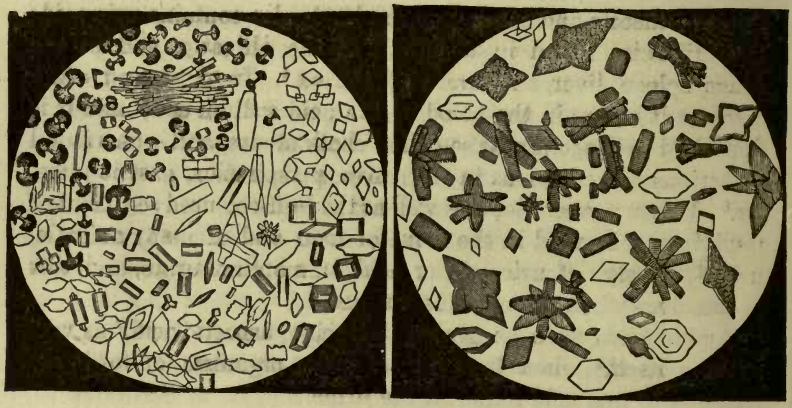


FIG. 111.

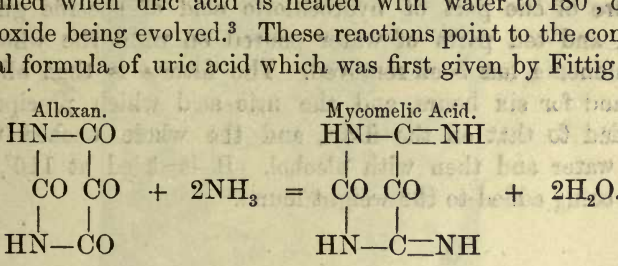
659 *Synthesis of Uric Acid.* Uric acid has recently been obtained synthetically. Strecker had noticed some time ago that, when heated with concentrated hydriodic acid to 160°—170°, uric acid decomposes into glycocoll, ammonia, and carbon dioxide,[2] the two latter compounds being products of decomposition of urea. Horbaczeweski has now made the interesting discovery, that when glycocoll is heated with an excess of urea to 200°—300°, uric acid is formed:[3]

$$C_2H_5NO_2 + 3CH_4N_2O = C_5H_4N_4O_3 + 3NH_3 + 2H_2O.$$

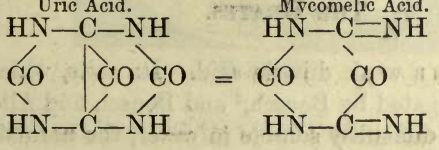
[1] Hofmann, *Rep. London Exhibition*, 1862, 118.
[2] *Zeitshr. Chem.* 1868, 215. [3] *Ber. Deutsch. Chem. Ges.* xv. 2678.

*Properties.* Uric acid consists of a crystalline powder of small scales or tables (Fig. 111), which become larger when slowly deposited from urine. It dissolves at 20° in from 14,000 to 15,000 parts, and at 100° in from 1,800 to 1,900 parts of water. It is insoluble in alcohol but tolerably soluble in glycerine, and it also dissolves without decomposition in strong sulphuric acid. On dry distillation uric acid decomposes without fusion, yielding ammonia, cyanic acid, cyanuric acid, and urea.[1] Scheele noticed that a solid acid is deposited on the sublimation of uric acid, and this he compared to succinic acid, whilst Pearson considered it to be benzoic acid. William Henry held the opinion that it was a peculiar acid, and this was confirmed, in the year 1820, by Lassaigne and Chevalier who termed it *pyro-uric acid*, and this was shown by Wöhler to be cyanuric acid. When oxidized in acid solution it yields urea and alloxan or mesoxalyl urea, $C_3O_3(NH)_2CO$, and when heated with ammonia, mycomelic acid, $C_2O(NH)_4CO$, is formed,[2] which latter compound is also obtained when uric acid is heated with water to 180°, carbon monoxide being evolved.[3] These reactions point to the constitutional formula of uric acid which was first given by Fittig:[4]

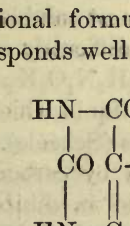
Alloxan. Mycomelic Acid.



Uric Acid. Mycomelic Acid.



Another constitutional formula for uric acid proposed by Medicus, which corresponds well with most of the reactions, is the following:



[1] Wöhler, *Pogg. Ann.* xv. 529 and 626.
[2] Wöhler and Liebig, *Ann. Chem. Pharm.* xxvi. 314.
[3] Wöhler, *Ann. Chem. Pharm.* ciii. 118; Hlasiwetz, *ib.* ciii. 211.
[4] *Grundr. Org. Chem.* 10 Aufl. 309; *Ber. Deutsch. Chem. Ges.* xi. 1792.

*Tests.* When uric acid is heated with a small quantity of nitric acid and evaporated to dryness, a pinkish residue is obtained, which, on addition of ammonia, yields a deep reddish-purple solution. Potash converts the colour into a violet blue. This reaction, which was first observed by Prout, will be explained under the head of Murexide.

If uric acid be dissolved in a drop of carbonate of soda solution, and then brought on to a piece of filter-paper moistened with a solution of silver nitrate, a dark brown stain of metallic silver is formed.[1]

*Estimation of Uric Acid.* In order to determine the quantity of uric acid contained in urine, 200 cc. of the liquid are mixed with 10 cc. of a saturated solution of carbonate of sodium, and after standing a few hours 20 cc. of concentrated sal-ammoniac solution are added, and the mixture allowed to stand for forty-eight hours longer in a cool place. The precipitate is collected on a weighed filter and washed two or three times, and then a mixture of one part of hydrochloric acid of specific gravity 1·123, and ten parts of water poured on until the whole of the ammonia has been removed. The filtrate is then allowed to stand for six hours, and the uric acid which precipitates is added to that on the filter, and the whole washed twice with water and then with alcohol. It is dried at 110°, 0·03 gram being added to the weight found.[2]

## The Urates.

660 Uric acid is a weak dibasic acid. Its salts, which have been chiefly investigated by Bensch,[3] and Bensch and Allen,[4] are for the most part difficultly soluble in water, the normal urates of the alkali metals being the most soluble; from these solutions carbon dioxide precipitates the difficultly soluble acid salts.

*Normal Potassium Urate,* $C_5H_2N_4O_3K_2$. Uric acid dissolves readily in potash ley forming a liquid which has a sweetish taste and which froths like soap-suds (Scheele). The normal salt is precipitated from this solution by carbon dioxide. It is also obtained by dissolving the acid in dilute caustic potash and evaporating the solution in a retort. The salt is obtained in

[1] Schiff, *Ann. Chem. Pharm.* cix. 67.
[2] Salkowski, *Fresenius' Zeitsch.* xvi. 371.
[3] *Ann. Chem. Pharm.* liv. 189. [4] *Ib.* lxv. 181.

needles or as a white crystalline meal. It possesses a strong alkaline reaction and a caustic taste, and it is gradually decomposed by boiling water with formation of the acid salt. Thirty-six parts of water at 15° dissolve one part of the salt, but it appears to be partially decomposed as the solution contains a small quantity of free caustic potash, and the undissolved residue contains the acid salt.

*Acid Potassium Urate*, $C_5H_3N_4O_3K$, is an amorphous or granular mass which dissolves at 20° in from 700 to 800 parts, and at 100° in from 70 to 80 parts of water. In fevers it occurs as a urinary deposit.

*Normal Sodium Urate*, $C_5H_2N_4O_3Na_2 + H_2O$, closely resembles the potassium salt, and forms hard nodules which dissolve with partial decomposition in 62 parts of water.

Fig. 112.

*Acid Sodium Urate*, $2C_5H_3N_4O_3Na + H_2O$, is formed not only by the action of carbon dioxide on the normal salt, but also when uric acid is boiled with carbonate of soda, borax, sodium phosphate, or sodium acetate. It is a crystalline powder exhibiting under the microscope the forms shown in Fig. 112, and dissolving at 15° in from 1100 to 1200 parts, and at 100° in from 123 to 125 parts of water. It occurs in amorphous grains as a urinary deposit, and also in gouty concretions.

*Acid Lithium Urate*, $C_5H_3N_4O_3Li$, crystallizes in grains and dissolves at 20° in 367·8 parts, and at 100° in 39 parts of water. The normal salt does not exist.[1]

[1] Schilling, *Ann. Chem. Pharm.* cxxii. 241.

The ready solubility of uric acid in carbonate of lithium is remarkable, inasmuch as this salt itself requires 200 parts of water for its solution. If, however, equal parts of uric acid and lithium carbonate be brought in contact with 90 parts of water at blood-heat, a clear solution is obtained, and at the boiling-point one part of the carbonate and no less than four parts of the acid dissolve. Owing to this property, lithium carbonate is much used in cases of gout or in other diseases in which deposits of uric acid are formed. Lipowitz, who made these observations, remarks that lithium is truly a *nomen et omen* when we remember its power of dissolving calculi.[1]

*Acid Ammonium Urate,* $C_5H_3N_4O_3(NH_4)$. This, as has been stated, occurs in many urinary concretions, and in the solid excrements of birds and serpents, and is formed when uric acid

Fig. 113.

is boiled with ammonia. It crystallizes in microscopic needles (Fig. 113) which dissolves at 15° in 1608 parts of water. When boiled for some time this solution loses all its ammonia.

The normal salt does not exist, but salts having the following composition are known:

(*a*) $C_5H_3N_4O_3(NH_4)+C_5H_2N_4O_3(NH_4)_2$ and

(*b*) $2C_5H_3N_4O_3(NH_4) + C_5H_2N_4O_3(NH_4)_2$.[2]

The *urates of other metals* either dissolve with more difficulty than the foregoing, or are altogether insoluble.

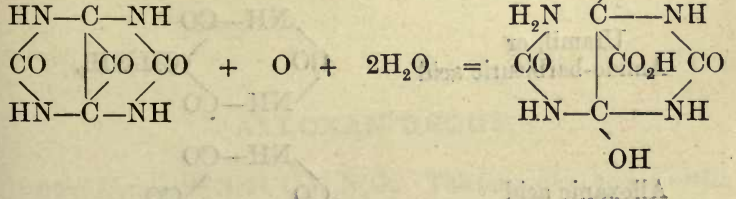
[1] *Ann. Chem. Pharm.* xxxviii. 352.
[2] Maly, *Journ. Prakt. Chem.* xcii. 10.

661 *Sulphates of Uric Acid.* By dissolving uric acid in hot sulphuric acid and cooling the solution Fritzsche obtained large transparent crystals having the formula $C_5H_4N_4O_3.4H_2SO_4$.[1] Löwe also obtained similar crystals, containing two molecules of sulphuric acid,[2] and Lassaigne, on dissolving in warm sulphuric acid the crystals which are first formed by saturation with uric acid at 100°, obtained on cooling large transparent crystals containing three molecules of sulphuric acid.[3]

*Methyl Uric Acid,* $C_5H_3(CH_3)N_4O_3$, is obtained by heating lead urate with methyl iodide to 150°—160°. It forms small thin prisms which dissolve in about 250 parts of boiling water, and are almost insoluble in cold water and boiling alcohol. It gives the murexide reaction, and when heated with hydrochloric acid under pressure it decomposes into carbon dioxide, ammonia, methylamine, and glycocoll, whilst on oxidation with nitric acid it yields methyl-alloxan. It is a dibasic acid, and forms, with the metals of the alkalis and alkaline earths, easily soluble salts.[4]

*Dimethyl Uric Acid,* $C_5H_2(CH_3)_2N_4O_3$, is obtained by heating basic lead urate with methyl iodide and forms small oblique prisms containing one molecule of water. It dissolves in about 200 parts of boiling- and 800 parts of cold-water, and is scarcely soluble in alcohol. On heating with hydrochloric acid it yields the same products as methyl uric acid, and on oxidation decomposes into methyl urea and methyl-alloxan, from which it appears that the two methyl groups are contained in two different urea-residues. It is also dibasic.[5]

*Uroxanic Acid,* $C_5H_8N_4O_6$, is formed when a solution of uric acid in caustic potash is exposed for some months to the action of air free from carbon dioxide, when the following reaction occurs :[6]



[1] *Journ. Prakt. Chem.* xiv. 243. [2] *Ib.* xcvii. 108.
[3] *Jahresb.* 1854, 469.
[4] Hill, *Ber. Deutsch. Chem. Ges.* ix. 370, 1090.
[5] Mabery and Hill, *Ber. Deutsch. Chem. Ges.* xi. 1329; xiii. 739.
[6] Stadeler, *Ann. Chem. Pharm.* lxxviii. 286; Strecker, *ib.* clv. 177; Mulder, *Ber. Deutsch. Chem. Ges.* viii. 1291.

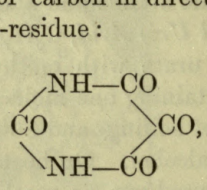
To this liquid, after standing, acetic acid and alcohol are added, when the potassium uroxanate is thrown down, and this is then decomposed with hydrochloric acid. This acid is difficultly soluble in cold water, and crystallizes in short prisms or sphenoids. On boiling with water it decomposes into carbon dioxide, urea and glyoxyl-urea.[1] Uroxanic acid is dibasic.

*Oxonic Acid,* $C_4H_5N_3O_4$, is formed together with uroxanic acid. It is a dibasic acid which is, however, not known in the free state, as its salts are decomposed even by acetic acid with formation of carbon dioxide, ammonia and glyoxyl-urea.[2]

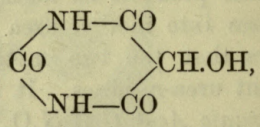
---

**662** The other numerous derivatives of uric acid may be classed in three groups. It has been stated that this acid when oxidized in acid solution first yields urea and *alloxan* or mesoxalylurea. This substance, as well as the bodies belonging to the *alloxan* group, contains three atoms of carbon in direct combination, and in addition to these a urea-residue:

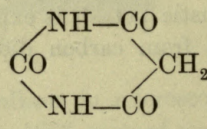
Alloxan, or Mesoxalylurea



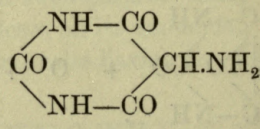
Dialuric acid, or Tatronylurea



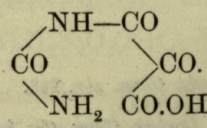
Barbituric acid, or Malonylurea



Uramil, or Amido-barbituric acid



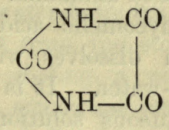
Alloxanic acid



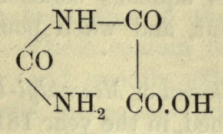
[1] Medicus, *Ber. Deutsch. Chem. Ges.* ix. 1162.
[2] *Ib. Ann. Chem. Pharm.* clxxv. 230.

Further oxidation converts alloxan into *parabanic acid* or oxalyl-urea. This substance, as well as the other compounds of the parabanic group, also contain one urea-residue or they are *mono-ureïdes*, as follows:

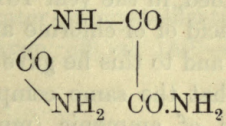
Parabanic acid, or oxalylurea



Oxaluric acid

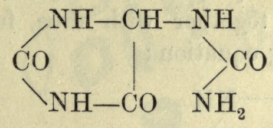


Oxaluramide, or Oxalan

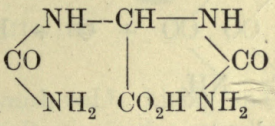


If, on the other hand, uric acid be oxidized in neutral or alkaline solution *allantoïn* is formed. This body is a *di-ureïde*, and from this the compounds arranged in the third group are derived:

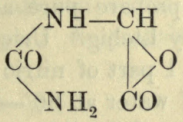
Allantoïn



Allantoic acid



Allanturic acid, or glyoxylurea

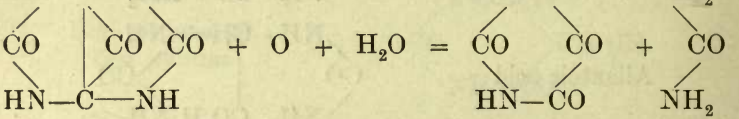


## ALLOXAN GROUP.

663 *Mycomelic Acid*, $C_4H_4N_4O_2$. The formation and constitution of this body have already been discussed. Its synthetic production is, however, a matter of great interest. Cyanogen and dry ammonia unite together to form *hydrazulmin*, $C_4H_6N_6$, a pitchblack amorphous mass which is decomposed by water into

*hydrazulmoxin* or *azulmic acid*, $C_4H_5N_5O$, which is also formed when an aqueous solution of cyanogen is allowed to stand (Vol. I., p. 659), or in larger quantity when the gas is passed into concentrated ammonia. If this be heated for a long time with water, mycomelic acid is formed.[1] It is a yellow light powder which dissolves with difficulty in cold- but more readily in hot-water. It is also easily soluble in alkalis and acids. Its aqueous solution fluoresces with a fine, greenish-blue colour, and when poured into water it forms sky-blue clouds.

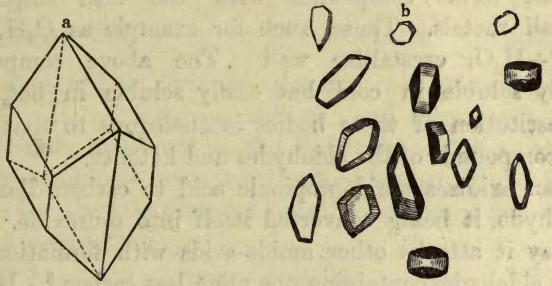
664 *Alloxan* or *Mesoxalyl-Urea*, $C_4H_2N_2O_4$. A crystalline body was obtained, in the year 1817, by G. Brugnatelli, by the action of nitric acid or of chlorine and iodine in presence of water upon uric acid, and to this he gave the name *Acido ossieretrico*.[2] Prout showed that the same compound is formed by the oxidation of purpurate of ammonia (murexide).[3] The mode of preparing this body seems to have been forgotten until Liebig and Wöhler pointed out the conditions under which it can be obtained in the pure state. They determined its composition and more important properties, and gave to it the name Alloxan.[4] It is formed, together with urea, from uric acid according to the following equation:



In order to prepare pure alloxan, the following method is recommended by Liebig.[5] Uric acid is added in small quantities to a mixture of 1 part of nitric acid of specific gravity 1·42, and 8 to 10 parts of water at 60°—70°, time being allowed between each addition for the solid to dissolve. As soon as the liquid has become a brick-red colour it is heated to boiling and filtered. To the filtrate, a concentrated solution of tin dichloride is added mixed with an equal volume of hydrochloric acid until the precipitation of alloxantin (p. 304), which takes place, is complete. This is then washed with cold water and dried on a porous plate. The dry mass is rubbed up, with a mixture

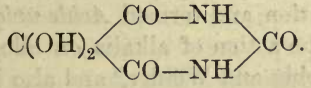
[1] Jacobsen and Emmerling, *Ber. Deutsch. Chem. Ges.* iv. 947.
[2] *Brugn. Giorn.* xi. 38 and 117; *Ann. Chim. Phys.* viii. 201; *Schweigg. Journ.* xxiv. 208.
[3] *Ann. Phil.* xiv. 363.
[4] *Ann. Chem. Pharm.* xxvi. 256.
[5] *Ann. Chem. Pharm.* cxlvii. 366.

of 2 parts of nitric acid of specific gravity 1·5 and 1 part of the same acid of specific gravity 1·42, to a thick paste, and the whole allowed to stand until the product is readily and completely soluble in water. The paste is then dried on a porous plate, heated in a water-bath till all the nitric acid is driven off, and crystallized from the smallest possible quantity of boiling water. On cooling a warm saturated solution, large crystals of alloxan, somewhat resembling those of heavy-spar in appearance, but belonging to the triclinic system,[1] are deposited (Fig. 114). These contain four molecules of water of crystallization and readily effloresce on exposure. The hot solution deposits monoclinic prisms (Fig. 115) containing one molecule of water of crystallization, which latter, according to Gmelin, is given off at 150°—160°, the




Figs. 114, 115.

residue becoming slightly brownish-red.[2] Liebig and Wöhler consider that the monohydrated alloxan is the anhydrous compound, but, according to Baeyer,[3] it probably possesses the following constitution:




Alloxan is easily soluble in water, and has a faint astringent taste. Its solutions redden litmus-paper, and stain the skin of a permanent purple-red colour, imparting to it a peculiar disagreeable smell. It is insoluble in nitric acid,

[1] Lang and Grailich, *Jahresb.* 1858, 308.
[2] *Handbook Org. Chem.* x. 173.
[3] *Gmelin-Kraut's Handb. Suppl.* 864.

and is therefore precipitated by this reagent from its aqueous solutions. In the pure state it can be preserved without undergoing decomposition, but if it contains nitric acid it decomposes with formation of alloxantin, oxalylurea, and other products, and a similar decomposition occurs when the aqueous solution is boiled. Heated with ammonia it forms a jelly-like mass of ammonium mycomelate. Ferrous salts impart a deep blue colour to solutions of alloxan. No precipitate is thrown down unless an alkali be present, in which latter case precipitation at once occurs. It was by this reaction that Liebig and Wöhler recognised that their compound was identical with Brugnatelli's *acido ossieretrico.* When boiled with water and lead oxide, alloxan is converted into carbon dioxide and urea.

Alloxan was found by Liebig to occur in mucus in a case of intestinal catarrh.[1]

Alloxan forms compounds with the acid sulphites of the alkali metals. These, such for example as $C_4H_2N_2O_4 + HKSO_3 + H_2O$, crystallize well. The above compound is difficultly soluble in cold, but easily soluble in hot, water.[2] The constitution of these bodies is analogous to that of the similar compounds of the aldehydes and ketones.

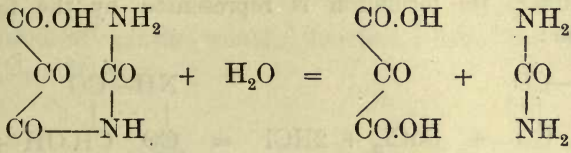
Alloxan oxidizes amidopropionic acid to carbon dioxide and acetaldehyde, it being converted itself into murexide. In the same way it attacks other amido-acids with formation of the isomeric aldehydes containing one atom less carbon.[3] If alloxan be heated with thio-urea and an alcoholic solution of sulphur dioxide, pseudo-thio-uric acid, $C_5H_6N_4O_3S$, is formed. This crystallizes in fine needles which are not soluble in water though easily soluble in alkalis.[4] Its constitution probably corresponds to that of pseudo-uric acid (p. 307).

665 *Alloxanic Acid,* $C_4H_4N_2O_5$, was first obtained by Vauquelin in an impure condition, and termed *Acide urique suroxigéné.* It is also formed by the action of alkalis on alloxan, and has been investigated by Liebig and Wöhler,[5] and also by Schlieper.[6] In order to prepare it, baryta-water is added drop by drop to a warm saturated solution of alloxan until a permanent turbidity is produced. This is then removed by the addition of a small quantity of alloxan, and the whole cooled. Barium alloxanate,

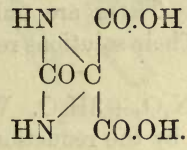
[1] *Ann. Chem. Pharm.* cxxi. 80.
[2] Gregory, *Phil. Mag.* [3], xxiv. 189; Wuth, *Ann. Chem. Pharm.* cviii. 41.
[3] Strecker, *ib.* cxxiii. 363.
[4] Nencki, *Ber. Deutsch. Chem. Ges.* iv. 722.
[5] *Ann. Chem. Pharm.* xxvi. 292. [6] *Ib.* lv. 263; lvi. 1.

$C_4H_2N_2O_5Ba+4H_2O$, then separates in short prisms or pearly scales, and the mother-liquor is again treated with baryta-water in a similar way. The salt is decomposed by dilute sulphuric acid, the solution concentrated over sulphuric acid, when a syrup remains, and this, on standing for some time, deposits a radiated crystalline mass consisting of hard triclinic needles.

Alloxanic acid possesses a strongly acid, and afterwards a sweetish, taste. It dissolves zinc with evolution of hydrogen, and decomposes carbonates and acetates. If the normal barium or calcium salt be boiled with water, urea and mesoxalic acid are formed:



According to this formula alloxanic acid contains only one carboxyl. It is, however, dibasic, and forms acid- normal- and basic-salts, inasmuch as the hydrogen of the amido-group, which is combined with two carbonyls, can be replaced by metals. On the other hand Claus[1] represents it as having the following constitution:

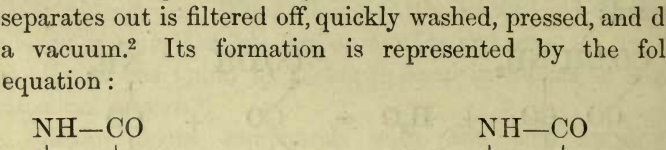


If this view be correct alloxan is the corresponding hydrate, and alloxanic acid should, therefore, be readily converted into this body; this is, however, not the case.

666 *Dialuric Acid* or *Tatronyl Urea*, $C_4H_4N_2O_4$. This compound is the final result of the action of reducing agents, such as zinc and hydrochloric acid, on alloxan. It may also be obtained by passing sulphuretted hydrogen gas into a boiling solution of alloxan until the separation of sulphur ceases (Liebig and Wöhler). The following is, however, the best method of preparation, impure uric acid being the raw material. On to 16 parts of this substance 32 parts of tolerably concentrated hydrochloric acid are poured, and 3 parts of finely powdered

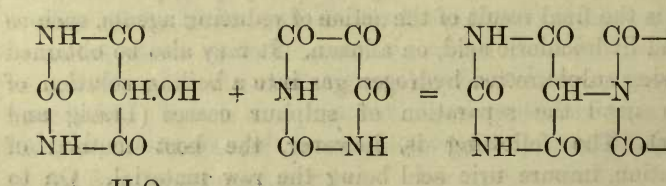
[1] *Ber. Deutsch. Chem. Ges.* vii. 232.

potassium chlorate gradually added, care being taken that the mass does not become too strongly heated, and that neither carbon dioxide nor chlorine is evolved. The paste of alloxan thus obtained is dissolved in a small quantity of warm water, and the solution filtered off from any undecomposed uric acid.[1] A quantity of metallic tin, equal in weight to the uric acid employed, is then dissolved in an excess of strong hydrochloric acid, and the hot solution added to the solution of alloxan, and then such a quantity of hydrochloric acid added that every 500 grams of the uric acid is made up to four liters of liquid. After standing for twenty-four hours the dialuric acid which separates out is filtered off, quickly washed, pressed, and dried in a vacuum.[2] Its formation is represented by the following equation:



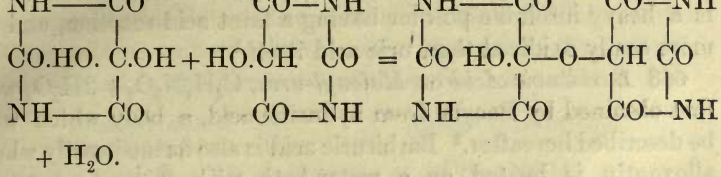
Dialuric acid crystallizes in short four-sided prisms, slightly soluble in cold water, and oxidizing in the moist state, on exposure to air, quickly to alloxantin. The acid is monobasic, ammonium dialurate and potassium dialurate being the only two salts known. These are anhydrous and difficultly soluble in cold water. Their solutions reduce silver nitrate even in the cold.

667 *Alloxantin*, $C_8H_4N_4O_7 + 3H_2O$. We have seen that alloxantin is formed not only by the reduction of alloxan but also by the oxidation of dialuric acid. It is moreover produced when equal molecules of dialuric acid and alloxan are brought together in concentrated solution,[3] this reaction being usually explained by the following equation:



[1] Schlieper, *Ann. Chem. Pharm.* lv. 253.
[2] Baeyer, *Ann. Chem. Pharm.* cxxvii. 12.
[3] Wöhler and Liebig, *Ann. Chem. Pharm.* xxvi. 279.

But in opposition to this view the fact must be remembered that when dimethylalloxan and dimethyldialuric acid, a reduction-product of the first named body, are brought together, anhydrous tetramethylalloxantin, $C_8H_2(CH_3)_4N_4O_8$, is produced. Hence the following equation more probably represents the formation of alloxantin:



$$+ H_2O.$$

Crystallized alloxantin would, therefore, have the formula $C_8H_6N_4O_8 + 2H_2O$.

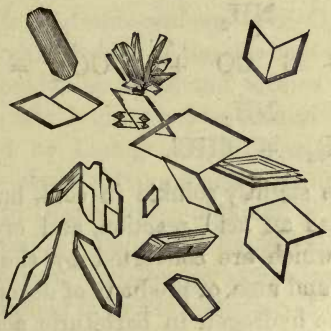


Fig. 116.

Its preparation has already been described under alloxan. It crystallizes in colourless or yellowish, small, oblique rhombic prisms or tables (Fig. 116). Alloxantin is also formed when ammonium dialurate is evaporated with an excess of dilute sulphuric acid, and the solution allowed to stand, when crystals of another form separate out, and for this reason Liebig and Wöhler believed it to be dimorphous. According to Gregory, however, these crystals are pseudomorphs of dialuric acid.[1]

Alloxantin is difficultly soluble in water; it colours litmus red, but does not form salts. It loses its water of crystallization at 150°, and becomes red in the air from absorption of

[1] *Phil. Mag.* xxiv. 188.

ammonia. Baryta-water gives a fine violet-blue precipitate, which becomes colourless on heating, from formation of the barium salts of dialuric acid and alloxanic acid. Alloxantin, reduces silver salts, selenium dioxide, osmic acid, &c., and when heated with dry ammonia it is converted into murexide.

If an aqueous solution of alloxantin and cyanamide be boiled, *iso-uric acid*, $C_5H_4N_4O_3$, is obtained, together with alloxan. It is a heavy insoluble powder having a faint acid reaction, and is more easily oxidized than uric acid itself.[1]

668 *Barbituric Acid* or *Malonyl-urea*, $C_4H_4N_2O_3 + 2H_2O$, was first obtained by Baeyer from hydurilic acid, a body which will be described hereafter.[2] Barbituric acid is also formed easily when alloxantin is heated on a water-bath with 3 to 4 parts of sulphuric acid until the evolution of sulphur dioxide ceases.[3] It may also be synthetically obtained by heating equal weights of malonic acid, urea, and phosphorus oxychloride to 100°:[4]

$$3\,CH_2(CO.OH)_2 + 3\,CO(NH_2)_2 + 2POCl_3 = 3\,CH_2\begin{<}CO—NH\\CO—NH\end{>}CO + 2PO(OH)_3 + 6HCl.$$

Malonyl-urea is slightly soluble in cold, but more readily in hot, water. It has an acid reaction, and crystallizes in large rhombic prisms which are converted by the action of alkalis into malonic acid and urea, or products of decomposition of these.

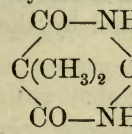
One atom of the hydrogen in barbituric acid may readily be substituted by metals. So-called normal salts are known, such, for instance, as silver barbiturate, $C_4H_2N_2O_3Ag_2$, a white, amorphous precipitate. Methyl iodide acts violently upon this substance with formation of *dimethyl-barbituric acid*, $C_4H_2N_2O_3(CH_3)_2$, a body which is difficultly soluble in cold water, but crystallizes from hot solution in glistening tablets. The fused mass boils at 265°, but the crystals melt at a much lower temperature. When this is decomposed by caustic potash malonic acid is not formed as might have been expected, but dimethyl-malonic acid (p. 256). Hence it appears that in barbituric acid the hydrogen atoms connected with carbon can be replaced by a metal. Dimethyl-barbituric acid has a faint acid reaction. When neutralized

[1] Mulder, *Ber. Deutsch. Chem Ges.* vi. 1236; vii. 1633.
[2] *Ann. Chem. Pharm.* cxxx. 136
[3] Finck, *ib.* cxxxii. 304.
[4] Grimaux, *Bull. Soc. Chim.* xxxi 146.

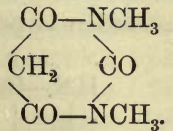
with ammonia and silver nitrate added, the hydrogen atoms which are combined with the nitrogen can also be replaced by a metal. Dimethyl-barbituric acid is also formed when dimethyl-malonic acid and urea are heated with phosphorus oxychloride.[1]

*Malonyl Dimethyl-urea* is a body isomeric with dimethyl-barbituric acid. It is obtained by the action of a mixture of malonyl chloride and phosphorus oxychloride on dimethyl urea, and crystallizes in flat needles melting at 123°, volatilizing without decomposition, and dissolving easily in water.[2] The following formulæ explain the isomerism of these two compounds:

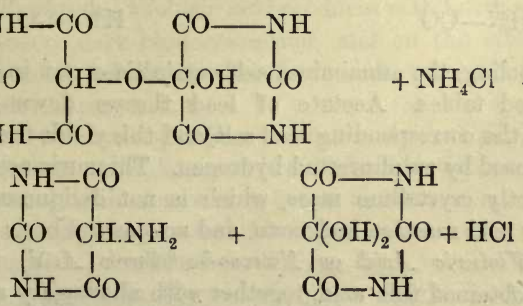
Dimethyl-malonyl Urea.
(Dimethyl-barbituic acid.)



Malonyl Dimethyl-urea.



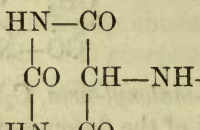
669 *Dialuramide* or *Amido-malonyl-urea*, $C_4H_5N_5O_3$, was first obtained by Prout as a product of the decompositon of purpurate of ammonia (murexide) by acids, and termed by him *purpuric acid*.[3] This name, which gives a false idea of the nature of the body, was changed by Liebig and Wöhler to *murexan*.[4] By boiling alloxantin with sal-ammoniac solution, or by boiling thionuric acid with water, they obtained a compound which they termed *uramil*.[5] Beilstein found that this body is identical with murexan,[6] and Baeyer ascertained its constitution inasmuch as he obtained it by the reduction of nitroso- and nitro-malonyl urea. Its formation from alloxantin may be rendered clear by the following equation:



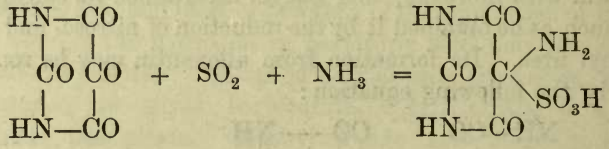
[1] Conrad and Gutzeit, *Ber. Deutsch. Chem. Ges.* xiv. 1643; Thorne, *Journ. Chem. Soc.* 1881, i. 543.
[2] Mulder, *Ber. Deutsch. Chem. Ges.* xii. 465.
[3] *Phil. Trans.* 1818, 420. *Ann. Chem. Pharm.* xxvi. 327.
[5] *Ib.* 274, 310, 323. [6] *Ib.* cvii. 176.

It forms silky needles insoluble in cold, but slightly soluble in hot, water.

*Pseudo-Uric Acid*, $C_5H_6N_4O_4$. When dialuramide is boiled with a solution of potassium cyanate the potassium salt of this acid is formed.[1] The ammonium salt is obtained by heating dialuramide with urea to 180°.[2] Hydrochloric acid precipitates the acid from solutions of its salts as a powder consisting of small prismatic crystals, which are difficultly soluble in hot water, dissolve readily in alkalis, but are decomposed by bromine or nitric acid into alloxan and urea, whilst on boiling with water and lead dioxide, carbon dioxide, oxalic acid, oxaluric acid (p. 319), and urea are formed. Pseudo-uric acid is monobasic, and its constitution is probably represented by the following formula:



*Thionuric Acid* or *Sulphaminbarbituric Acid*, $C_4H_5N_3SO_6$. This substance was obtained by Liebig and Wöhler by mixing ammonium sulphite with an excess of ammonium carbonate, and adding to this a solution of alloxan, slowly heating to the boiling point, and allowing it to boil for half an hour:[3]

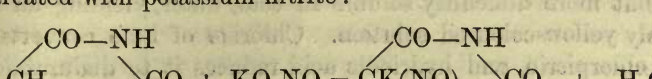


On cooling, the ammonium salt crystallizes out in glistening, four-sided tables. Acetate of lead throws down from this solution the corresponding lead salt, and this yields the acid when decomposed by sulphuretted hydrogen. Thionuric acid forms an indistinctly crystalline mass, which is not deliquescent, has a strongly acid reaction and taste, and acts as a dibasic acid.

670 *Violuric Acid* or *Nitroso-barbituric Acid*, $C_4H_3N_3O_4$. Baeyer obtained this acid, together with alloxan, by acting with nitrous acid or dilute nitric acid on hydurilic acid. Its potassium

[1] Baeyer, *Ann. Chem. Pharm.* cxxvii. 3
[2] Grimaux, *Bull. Soc. Chim.* xxxi. 535.
[3] *Ann. Chem. Pharm.* xxvi. 268.

salt is formed when a solution of hydurilic or of barbituric acid is treated with potassium nitrite :[1]



The acid is tolerably soluble in cold water, readily so in hot water and in alcohol, and crystallizes in glistening rhombic pyramids containing one molecule of water which is driven off at 100°. Its solution decomposes on heating above 60°, and when treated with bleaching powder yields chlorpicrin. Ammonium sulphite converts it into thionuric acid, and when heated with potash it decomposes into nitroso, malonic acid, carbon dioxide, and ammonia, whilst in contact with hydriodic acid or sulphuretted hydrogen it yields dialuramide. Violuric acid is monobasic, and decomposes the acetates. Its salts are characterized by their splendid and varying colours.

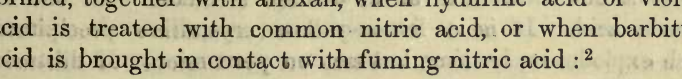
*Potassium Violurate*, $C_4H_2N_3O_4K + 2H_2O$, crystallizes in deep blue scales or prisms, which are more soluble in hot than in cold water, yielding a violet-blue coloured solution. When thrown into hot concentrated hydrochloric acid, colourless prisms of the compound, $2(C_4H_3N_3O_4,KCl) + HCl + 6H_2O$, separate out. These, when treated with potassium acetate, are converted into the ordinary salt.

*Barium Violurate*, $(C_4H_2N_3O_4)_2Ba + 4H_2O$, yields glistening red quadratic tables, almost insoluble in cold water.

*Magnesium Violurate*, $(C_4H_2N_3O_4)\,Mg + 6H_2O$, is also very difficultly soluble, and forms oblique purple-red crystals.

*Ferrous Violurate.* Violuric acid produces with ferrous acetate solution a deep, dark-blue coloration, and on the addition of alcohol six-sided tables of the above salt, possessing a red metallic lustre, separate out.

671 *Dilituric Acid* or *Nitrobarbituric Acid*, $C_4H_3N_3O_5$, is formed, together with alloxan, when hydurilic acid or violuric acid is treated with common nitric acid, or when barbituric acid is brought in contact with fuming nitric acid :[2]



[1] *Ann. Chem. Pharm.* cxxvii. 20 ; cxxx. 140.
[2] Baeyer, *Ann. Chem. Pharm.* cxxvii. 211.

It crystallizes in square prisms, which are easily soluble in hot, but more difficultly soluble in cold, water, yielding an intensely yellow-coloured solution. Chloride of lime converts it into chlorpicrin, and hydriodic acid reduces it to dialuramide, but sulphuretted hydrogen does not act upon it. It is a tribasic acid, but its characteristic salts are those containing one equivalent of metal. Most of these are explosive, but they are so stable that they are not decomposed by a mineral acid. The barium salt is not decomposed even by dilute sulphuric acid, though precipitated by sulphates. The following are the most characteristic compounds.

*Monhydric Potassium Dilituratе*, $C_4HN_3O_5K_2$. Dilituric acid dissolves in caustic potash yielding a citron-yellow coloured solution, and on adding alcohol to the hot liquid fine yellow needles, grouped in nodular masses, are deposited. This salt is insoluble in concentrated caustic potash, and detonates slightly on heating, pure potassium cyanate remaining behind. If concentrated sulphuric acid be added to it, explosions occur, and hydrochloric acid converts it into the di-hydric salt, $C_4H_2N_3O_5K$, which is always formed when dilituric acid is brought in contact with a potassium salt. This is scarcely soluble in cold, and difficultly soluble in hot, water, and separates from dilute solution in cubes.

*Dihydric Ammonium Dilituratе*, $C_4H_2N_3O_5(NH_4)$, is a precipitate consisting of microscopic prisms, which are formed when dilituric acid is brought into contact with ammonia or an ammonium salt.

*Ferrous Dilituratе*, $(C_4H_2N_3O_5)_2Fe + 8H_2O$, is obtained by the addition of dilituric acid to a solution of ferrous sulphate and forms a precipitate, consisting of needles which have a faintly greenish colour and are very difficultly soluble in water. They explode when heated above 120°.

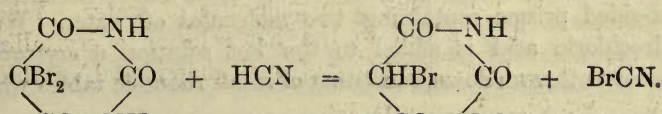
*Normal Silver Dilituratе*, $C_4N_3O_5Ag_3$, is formed when an excess of a hot solution of silver acetate is mixed with one of dilituric acid. It is a lemon-yellow crystalline precipitate which explodes on heating, but not on percussion. If dilituric acid be employed in excess, or if the acid be added to a silver nitrate solution, the acid salt, having the formula $C_4H_2N_3O_5Ag$, is thrown down. This is tolerably soluble in hot water and crystallizes in prisms.

672 *Violantin*, $C_8H_6N_6O_9 + 4H_2O$, is obtained by mixing hot concentrated solutions of violuric acid and dilituric acid, which

then combine directly together. It is, therefore, also formed when hydurilic acid is warmed with weak nitric acid. It is a yellowish-white granular crystalline powder which on recrystallization from water is again converted into its constituents. On the other hand, it can be recrystallized from glacial acetic acid or from dilute alcohol, when only a partial decomposition takes place. With ammonia it yields a blue colour, and with magnesium acetate it forms a fine blue crystalline precipitate, whilst magnesium violurate is red. Other salts generally decompose it into its constituents. Thus with potassium acetate it yields a precipitate of acid potassium dilituarate, whilst, later, potassium violurate crystallizes out.[1]

*Dibrombarbituric Acid*, $C_4H_2Br_2N_2O_3$, was originally described by Baeyer as alloxan bromide. It is formed by the action of bromine on barbituric acid, nitroso- and nitro-barbituric acid, and hydurilic acid, which at the same time also yield alloxan. It is difficultly soluble in cold, but dissolves more readily in hot, water, the solution decomposing on boiling with formation of alloxan and a volatile body which violently attacks the eyes and mucous membranes. In order to prevent this decomposition it is crystallized from dilute nitric acid solution, when rhombic prisms or tables are deposited, and it crystallizes in the same form from a solution in alcohol, in which it is easily soluble. It fuses on heating with evolution of bromine vapours yielding a liquid which, on cooling, solidifies to a crystalline mass. Bromine converts it into tribromacetyl-urea, which is also formed by the action of alkalis, and it is decomposed on heating with formation of bromoform.[2] When sulphuretted hydrogen gas is passed for some time into a solution of dibrombarbituric acid heated to 90° it is converted into alloxantin.[3]

*Monobrombarbituric Acid*, $C_4H_3BrN_2O_3$, is formed by the action of zinc or sodium-amalgam and water on the foregoing compound, and is also produced by the action of hydrocyanic acid, which in the anhydrous condition dissolves the dibrom-acid without alteration, but when diluted acts upon it as follows:




[1] Baeyer, *Ann. Chem. Pharm.* cxxvii. 223.
[2] *Ib.* cxxvii. 229; cxxx. 130.
[3] Grimaux, *Bull. Soc. Chim.* xxxi. 146.

It forms crystalline crusts consisting of small needles, is difficultly soluble in cold water, and is a monobasic acid which decomposes the acetates.[1]

673 *Hydurilic Acid*, $C_8H_6N_4O_6$. This compound, which has been often mentioned in the foregoing pages, can be prepared in a variety of ways. Schlieper was the first to prepare the acid ammonium salt, together with alloxan, by the action of dilute nitric acid or uric acid.[2] It is also formed when alloxan or alloxantin is heated for some time with very dilute sulphuric acid,[3] or when dialuric acid is heated with glycerin to a temperature of 140°—150°. The glycerin acts here merely as a solvent, and two reactions occur at the same time, inasmuch as four molecules of dialuric acid are converted into hydurilic acid and a fifth into formic acid, carbon dioxide, and ammonia :[4]

(1) $4C_4H_4N_2O_4 = 2C_8H_6N_4O_6 + 2H_2O + O_2$.

(2) $C_4H_4N_2O_4 + 2H_2O + O_2 = 3CO_2 + CH_2O_2 + 2NH_3$.

Hydurilic acid is also formed, together with glycocoll and carbon dioxide, when uric acid is heated to 110°—130° with sulphuric acid.[5]

It is, however, best obtained when hydrated alloxantin is heated to 170° in a heated tube :

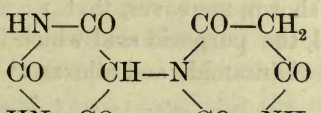
$$2C_8H_4N_4O_7 + 6H_2O = C_8H_6N_4O_6 + 4NH_3 + C_2H_2O_4 + 2CO + 4CO_2.$$

When heated in an open vessel the same reaction occurs, but the oxalic acid is converted into carbon monoxide, carbon dioxide, and water. Alloxan can also be converted in this way into hydurilic acid, but only in closed vessels, as otherwise the water necessary for the reaction escapes.[6] It is also formed together with barbituric acid when dibrombituric acid is treated with hydriodic acid.

Hydurilic acid is very difficultly soluble in cold, but dissolves somewhat more readily in hot, water, crystallizing in small four-sided prisms containing two molecules of water. When hydrochloric acid is added to the hot solution a crystalline powder is thrown down, consisting of small rhombic tables which

[1] Baeyer, *Ann. Chem. Pharm.* cxxx. 134.
[2] *Ann. Chem. Pharm.* lvi. 11.
[3] Finck, *Ib.* cxxxii. 303.
[4] Baeyer, *Ib.* cxxvii. 14.
[5] Schultzen and Filehne, *Ber. Deutsch. Chem. Ges.* i. 150.
[6] Murdoch and Döbner, *Ib.* ix. 1102.

contain one molecule of water. Hydrochloric acid precipitates hydurilic acid from alkaline solutions in the form of a chalk-like amorphous powder which, when allowed to stand with hot water or hot hydrochloric acid, soon becomes crystalline. It is a strong dibasic acid decomposing most of the metallic chlorides with formation of acid salts, whilst acetates, with the exception of potassium and ammonium acetates, are decomposed by it with formation of the normal salts. A characteristic reaction of this acid and its salts is the property which they possess of colouring ferric chloride a splendid green, which on heating is converted into a red, and is destroyed by alkalis or strong acids. The decompositions of hydurilic acid which have been described in the preceding pages render it probable that it possesses the following constitution:



674 *Purpuric Acid*, $C_8H_5N_5O_6$. Prout, in his investigation on the "pathology of urine," examined the purple-red substance obtained by evaporating uric acid with nitric acid, and he found that, when the solution is neutralized with ammonia and slowly evaporated, a granular, dark-red, crystalline mass is obtained, reflecting light with a purple colour. To this he gave the name of purpurate of ammonia, and he prepared other purpurates by double decomposition with metallic salts. By the action of an acid he obtained from these a colourless compound which he considered to be free purpuric acid.[1] Wöhler and Liebig then showed that this body, which they termed murexan, is not the only product of the decomposition, and that it does not give any dark red salts with bases. They considered, therefore, that purpurate of ammonia is an amide having a complicated composition, and they termed it *murexide* (from *murex*, the shell from which the purple-tyrian dye is said to have been obtained).[2] Soon afterward a memoir by Fritzsche appeared, in which he defended Prout's view, and gave the results of a more complete investigation of the purpurates, proposing for murexide or purpurate of ammonia a

[1] *Phil. Trans.* 1818, 420.

[2] *Ann. Chem. Pharm.* xxvi. 319. See also Schunck "On the Purple of the Ancients," *Chem. Soc. Journ.* xxxv. 589.

formula different from that which Wöhler and Liebig gave as the correct one.[1] Liebig, however, did not agree with these views,[2] so that Gmelin, who was then writing this portion of his *Handbook*, undertook the examination of these contradictory statements, and endeavoured from analysis to obtain a formula which should explain the formation and decompositions of murexide. According to the view which he held to be the most probable, murexide should be formed by the action of ammonia on alloxantin, and experiment verified this prediction :[3]

$$C_8H_4N_4O_7 + 2NH_3 = C_8H_8N_6O_6 + H_2O.$$

This formula, as well as the view that murexide is the ammonium salt of purpuric acid, then became generally adopted, and this has been since verified by the investigations of Beilstein, who has shown, moreover, that when a purpurate is treated with an acid, the purpuric acid which is liberated is at once converted into dialuramide and alloxan :[4]

$$C_8H_5N_5O_6 + H_2O = C_4H_5N_3O_3 + C_4H_2N_2O_4.$$

Purpuric acid chiefly forms acid salts (Beilstein).

675 *Acid Ammonium Purpurate*, or *Murexide*, $C_8H_4N_5O_6(NH_4) + H_2O$. In addition to the methods which have already been described, this body can also be obtained when a solution of alloxan and alloxantin is treated with ammonia (Liebig and Wöhler). In order to prepare it in this way, 4 parts of alloxantin and 7 parts of alloxan containing 4 molecules of crystallization-water are dissolved in 240 parts of hot water, and 80 parts of a cold saturated solution of ammonium carbonate added.[5] It is also formed when an ammoniacal solution of dialuramide is exposed to the air or heated with mercuric oxide :

$$2C_4H_5N_3O_3 + HgO = C_8H_8N_6O_6 + H_2O + Hg.$$

Or, according to Beilstein, 4 parts of dialuramide and 3 parts of mercuric oxide are boiled with a sufficient quantity of water and some ammonia.

Murexide crystallizes in four-sided prisms, the faces of which possess a splendid green metallic lustre like that of the wing-cases of the rose-beetle and other insects. By transmitted

[1] *Journ. Prakt. Chem.* xvi. 380 ; xvii. 42.
[2] *Ann. Chem. Pharm.* xxxiii. 120.
[3] *Handbook*, x. 195.
[4] *Ann. Chem. Pharm.* cvii. 176.
[5] Liebig, *Organ. Chem.* 232.

light they appear of a garnet-red colour, and when pulverized yield a red powder which, when rubbed, exhibits a bright green metallic reflection. It dissolves with difficulty in cold, but more easily in hot, water, yielding a purple-red coloured solution, and is insoluble in alcohol and ether.

About twenty-five years ago murexide was used in dyeing and calico-printing works in such quantity that the factory of Mr. Rumney in Manchester turned out 12 cwt. per week, for which quantity twelve tons of guano was required. The manufacture of murexide was, however, only a shortlived one, inasmuch as it was soon supplanted by the cheaper and equally brilliant coal-tar colours.

*Acid Potassium Purpurate*, $C_8H_4N_5O_6K$, is obtained by decomposing murexide with nitre, or by exposing a solution of dialuramide in cold caustic potash to the air. It is very similar to murexide. Its solution, as well as that of murexide, is coloured deep blue by caustic potash, and alcohol precipitates a thick blue liquid which is probably the normal salt.

*Acid Silver Purpurate*, $2C_8H_4N_5O_6Ag + 3H_2O$. On adding silver nitrate to a solution of murexide acidified with nitric acid, this salt is thrown down as a light purple-red powder. The normal salt, $C_8H_3N_5O_6Ag_2$, which was obtained accidentally by Beilstein by precipitating a cold saturated solution of murexide with a neutral solution of silver nitrate, is a fine brownish-red powder.

The *calcium* and *barium salts* are dark-green crystalline precipitates, dissolving but slightly in water, and yielding a purple-coloured solution. Lead acetate gives a red precipitate with murexide solution, and corrosive sublimate a blood-red, and mercurous nitrate a violet precipitate. These reactions were used in calico-printing to fix the murexide colour, and the violet tints were obtained by fixing the colour on the cloth with corrosive sublimate in a bath which contained oxalic acid and sodium acetate, when a reduction occurred (Beilstein).

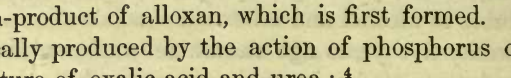
## PARABANIC GROUP.

676 *Parabanic Acid*, or *Oxalyl Urea*, $C_3H_2N_2O_3$, was first obtained by Liebig and Wöhler, by acting with tolerably concentrated hot nitric acid on uric acid.[1] It is also formed when

[1] *Ann. Chem. Pharm.* xxvi. 285.

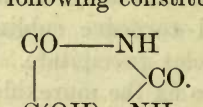
uric acid is warmed with hydrochloric acid and potassium chlorate,[1] or boiled with manganese dioxide and dilute sulphuric acid.[2]

Parabanic acid is likewise produced when bromine and water act upon uric acid;[3] the acid in all these cases being an oxidation-product of alloxan, which is first formed. It may be synthetically produced by the action of phosphorus oxychloride on a mixture of oxalic acid and urea:[4]



In order to prepare it, 1 part of uric acid is added, in small portions at a time, to 3 parts of nitric acid of specific gravity 1·30 heated to 70°. The solution is first concentrated over the lamp, and then evaporated to dryness on the water-bath, and the residue is recrystallized from water.[5] It is also easily obtained by pouring a small quantity of water on to uric acid and adding an excess of bromine.[6] It crystallizes in flat, transparent, monoclinic prisms or needles (see Fig. 117), which dissolve at 8° in 21·2 parts of water, and have a strongly acid taste.

When one part of pure uric acid is slowly added to 3 parts of nitric acid heated to 60°, the temperature kept at 35°—55°, and at last the liquid heated to 70°, large crystals, having the composition $C_3H_2N_2O_3+H_2O$, separate out on warming the solution. These dissolve at 8° in 7·4 parts of water, and between 150°—160° lose their water of crystallization and then crystallize from solution in water in the anhydrous condition. This hydrate probably possesses the following constitution:[7]



Parabanic acid is dibasic, although it has a tendency to form acid salts. Those of the alkali-metals are very unstable, and are easily converted into the salts of oxaluric acid (p. 319). The normal silver salt, having the composition $C_3Ag_2N_2O_3+H_2O$,

[1] Gerhardt and Laurent, *Ann. Chim. Phys.* [3], xxiv. 175.
[2] Wheeler, *Zeitsch. Chem.* 1866. 746.
[3] Hardy, *Jahresb.* 1864, 631.
[4] Ponomarew, *Bull. Soc. Chim.* xviii. 97.
[5] Menschutkin, *Ann. Chem. Pharm.* clxxii. 74.
[6] Magnier, *Bull. Soc. Chim.* xxii. 56.
[7] Tollens and Wagner, *Ann. Chem. Pharm.* clxvi. 321; Tollens, *ib.* clxxv. 227.

is very characteristic, being obtained as a crystalline precipitate by adding silver nitrate to a solution of the acid.

*Oxalyl-diureïde*, $C_4H_6N_4O_4$, is a slightly soluble powder, obtained by heating parabanic acid with urea. Hence it possesses the following constitution :[1]

$$\begin{array}{l} CO—NH_2 \qquad\quad CO.NH_2 \\ | \qquad\qquad\quad | \\ CO—NH—CO—NH. \end{array}$$

677 *Methyl-parabanic Acid*, $C_3H(CH_3)N_2O_3$, was first obtained from creatinine, which is converted by nitrous acid into the base

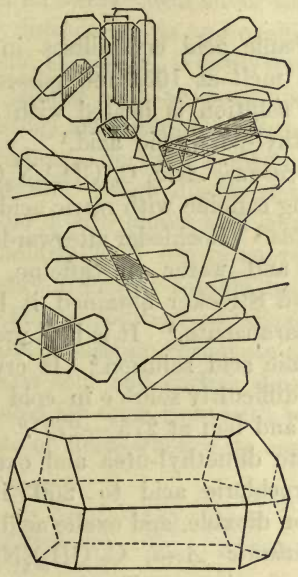


Fig. 117.

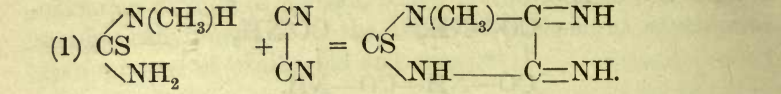
$C_4H_8N_4O_2$; and this, when heated with hydrochloric acid, decomposes into ammonia and methyl-parabanic acid.[2] This latter compound is also formed by the oxidation of methyl-uric acid with nitric acid.[3] It crystallizes from hot water in glistening needles or prisms, which melt at 149°·5, and its solution has a feeble acid reaction. Alkali decomposes it into oxalic acid and methyl-urea.

[1] Grimaux, *Bull. Soc. Chim.* xxxii. 120.

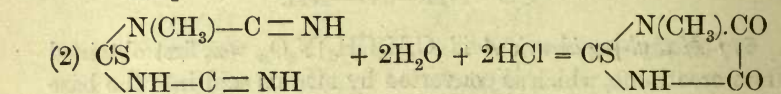
[2] Dessaignes, *Ann. Chem. Pharm.* xcvii. 342 ; Strecker, *ib.* cxviii. 164 ; Märcker, *ib.* cxxxiii. 315.

[3] Hill, *Ber. Deutsch. Chem. Ges.* ix. 1093.

*Methyl-thioparabanic Acid*, $C_3H(CH_3)N_2SO_2$. If cyanogen gas be passed into an alcoholic solution of methyl-thio-urea, a crystalline compound is formed, which, on evaporation, passes into the above compound, the following reaction occurring:



(1) $CS(N(CH_3)H)(NH_2) + (CN)_2 = CS(N(CH_3)—C{=}NH)(NH——C{=}NH)$.



(2) $CS(N(CH_3)—C{=}NH)(NH—C{=}NH) + 2H_2O + 2HCl = CS(N(CH_3).CO)(NH——CO) + 2NH_4Cl$.

Methyl-thioparabanic acid crystallizes in very thin, bright green scales, which melt at 105°, and possess an acid reaction. When its aqueous solution is heated with silver nitrate, it is converted into methyl-parabanic acid.[1]

678 *Dimethyl-parabanic Acid*, $C_3(CH_3)_2N_2O_3$, was obtained by Stenhouse by boiling caffeine with nitric acid, and was described by him as *nitro-theïne*.[2] Rochleder afterwards prepared it by the action of chlorine and water on caffeine, and he termed it *cholestrophane*;[3] and Strecker obtained it by heating methyl iodide with silver parabanate.[4] It is best prepared by oxidizing caffeine with chromic acid solution.[5] It crystallizes in pearly laminæ, which are difficultly soluble in cold water and alcohol, and melt at 145°·5 and boil at 275°—277°.[6] It is easily decomposed by alkalis into dimethyl-urea and oxalic acid, and when heated with hydrochloric acid to 200° it decomposes into methylamine, carbon dioxide, and oxalic acid.[7]

*Dimethyl-thioparabanic Acid*, $C_3(CH_3)_2N_2SO_2$, is obtained from dimethyl-thio-urea in a similar manner to the monomethyl compound. It crystallizes in six-sided scales, having a colour like that of yellow chromate of potash. These melt at 112°·5, are slightly soluble in cold, but dissolve more readily in hot, water, and have a neutral reaction. When heated with silver nitrate, the solution is converted into dimethyl-parabanic acid.

*Reactions for the Parabanic Acids.* All these acids can be recognized by the following reaction. To the aqueous solution

[1] Andreasch, *Ber. Deutsch. Chem. Ges.* xiv. 1447.
[2] *Chem. Soc. Mem.* i. 215, 237. [3] *Ann. Chem. Pharm.* lxxiii. 57.
[4] *Ib.* cxviii. 174. [5] Maly and Hinteregger, *Monats. Chem.* ii. 88.
[6] Menschutkin, *Ann. Chem. Pharm.* clxxviii. 202.
[7] Calem, *Ber. Deutsch. Chem. Ges.* xii. 624.

calcium chloride and ammonia are added and the liquid warmed, when calcium oxalate separates out (Andreasch).

*Oxalantin*, $C_6H_4N_4O_5 + H_2O$, was first prepared by Schlieper, in small quantities together with allanturic acid by boiling alloxantic acid for some time with water, and was termed by him leucoturic acid.[1] Its zinc salt is formed by treating parabanic acid with zinc and hydrochloric acid in the cold;[2] it is difficultly soluble, and is easily decomposed by sulphuretted hydrogen. Oxalantin thus obtained forms a hard crystalline crust difficultly soluble in water, and has a faint acid reaction. Boiling nitric acid is without action upon this body; it reduces metallic silver from an ammoniacal silver solution, whilst alkalis decompose it easily into ammonia and oxaluric acid.

679 *Oxaluric Acid*, $C_3H_4N_2O_4$, is easily formed when parabanic acid is heated to boiling with aqueous ammonia (Liebig and Wöhler). On cooling, ammonium oxalurate separates out in glistening, silky needles. This salt is also found in small quantities in human urine.[3] When dissolved in a small quantity of warm water, and hydrochloric acid added, and the whole quickly cooled, oxaluric acid separates out as a crystalline powder, which is very difficultly soluble in cold water, and has an acid taste. When a solution of alloxan is treated with hydrocyanic acid, and potassium carbonate added, oxaluric acid, together with dialuric acid and carbon dioxide, is formed.[4] If oxaluric acid be boiled for some time with water, it is converted into the acid oxalate of urea, whence its name:

$$\begin{array}{l} CO.OH \quad NH_2 \\ | \qquad\quad | \\ CO{-}NH{-}CO \end{array} + H_2O = \begin{array}{l} CO.OH \quad NH_2 \\ | \qquad\quad | \\ CO.O.NH_3{-}CO. \end{array}$$

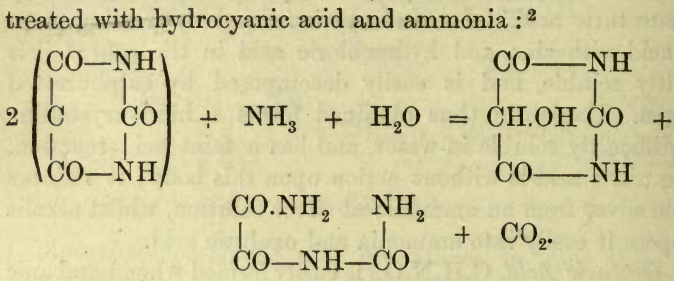
When heated with phosphorus oxychloride, it is reconverted into parabanic acid.[5] It is monobasic, and its salts have been carefully examined by Waage.[6]

*Ethyl Oxalurate*, $C_3H_3N_2O_4(C_2H_5)$, was obtained by Henry by acting with ethyl oxalyl chloride on urea.[7] Grimaux obtained it from silver oxalurate and ethyl iodide.[8] It is almost insoluble in cold water, and crystallizes from warm water in

[1] *Ann. Chem. Pharm.* lvi. 2.
[2] Limpricht, *ib.* cxi. 134.
[3] Schunck, *Proc. Roy. Soc.* xv. 258.
[4] Strecker, *Ann. Chem. Pharm.* cxiii. 53.
[5] Grimaux, *Ann. Chim. Phys.* [5], xi. 367.
[6] *Ann. Chem. Pharm.* cxviii. 301.
[7] *Ber. Deutsch. Chem. Ges.* iv. 644.
[8] *Bull. Soc. Chim.* xxi. 157.

thin, silky needles. If a few drops of ammonia be added to the hot solution, and then silver nitrate added, a precipitate of silver parabanate is formed.[1]

*Oxaluramide*, or *Oxalan*, $C_3H_5N_3O_2$, is formed, together with carbon dioxide and dialuric acid, when a solution of alloxan is treated with hydrocyanic acid and ammonia :[2]



This reaction corresponds to the formation of dialuric acid from alloxan. In both cases the hydrocyanic acid remains unchanged.

Oxaluramide is also formed when urea is fused with ethyl oxamate (p. 120),[3] or when ethyl oxalurate is heated with alcoholic ammonia (Salomon). It is a crystalline powder which is insoluble in cold water and when boiled with water it is converted into ammonium oxalurate. It dissolves in concentrated sulphuric acid without change, and is again precipitated from solution by water.

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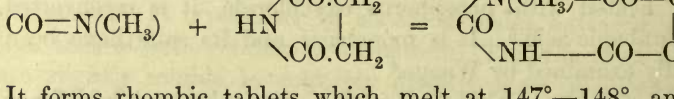
680 The following compounds, though not derivatives of uric acid, may be conveniently described here.

*Methyl Succinyl Urea*, $C_6H_8N_2O_3$. Methyl carbimide combines violently with succinimide to form this compound :

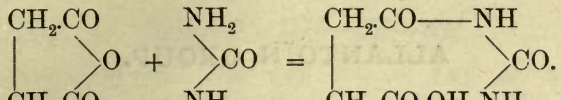


It forms rhombic tablets which melt at 147°—148°, and are slightly soluble in cold water and alcohol.

The corresponding ethyl compound is a similar body melting at 94°—95°, easily soluble in water and alcohol, and decomposing, when heated from 150°—160° again into ethyl carbimide and succinimide.[4]

[1] Salomon, *Ber. Deutsch. Chem. Ges.* ix. 374.
[2] Schischkow and Roesing, *Ann. Chem. Pharm.* cvi. 255 ; Strecker, *ib.* cxiii. 48.
[3] Carstanjen, *Journ. Prakt. Chem.* [2], ix. 143.
[4] Menschutkin, *Ann. Chem. Pharm.* clxxviii. 204.

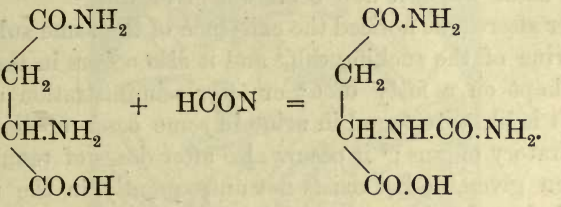
*Succinuric Acid*, $C_5H_8N_2O_4$, is formed by heating urea with succinic anhydride:



It is a monobasic acid, almost insoluble in cold water, and crystallizing from hot water in scales.[1]

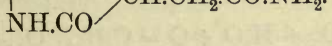
*Succinyl Dicarbamide*, $C_2H_4(CO.NH.CO.NH_2)_2$, is obtained by heating two molecules of urea with rather more than one molecule of succinyl chloride. It is a powder, difficultly soluble in hot water and almost insoluble in alcohol.[2]

*Amidosuccinuric Acid*, $C_5H_9N_3O_4$, is formed by evaporating a solution of asparagin and potassium cyanate and treating the residue with hydrochloric acid:



It is almost insoluble in alcohol, and crystallizes from water in hard prisms.[3]

*Malyl Ureïde*, $C_5H_7N_3O_3$, is formed by heating asparagin with urea to 125°—130°. It crystallizes from hot water in oblique rhombohedrons.[4] Its constitution is probably:



When this body or amidosuccinuric acid is boiled with hydrochloric acid, *malyl ureïdic acid*, $C_5H_6N_2O_4$, is formed. This is also formed by heating aspartic acid with urea.[5] It is easily soluble in water, and crystallizes in prisms.

[1] Pike, *Ber. Deutsch. Chem. Ges.* vi. 1104.
[2] Conrad, *Journ. Prakt. Chem.* [2], ix. 301.
[3] Guareschi, *Ber. Deutsch. Chem. Ges.* x. 1747.
[4] Grimaux, *Ann. Chim. Phys.* [5], xi. 400.
[5] Guareschi, *Ber. Deutsch. Chem. Ges.* ix. 1435.

## ALLANTOÏN GROUP.

681 *Allantoïn*, $C_4H_6N_4O_3$. This compound was discovered by Vauquelin and Buniva in the amniotic liquid of the cow, and termed by them amniotic acid.[1] Neither Dzondi nor Prout could obtain it, and then Lassaigne showed that it is contained not in the amniotic, but in the allantoic, liquid, which latter fluid was mixed with the amniotic fluid examined by the first-named chemists, and he termed the body *acide allantoïque*.[2] It was first artificially prepared and carefully investigated by Liebig and Wöhler, and, as Gmelin had already shown that the substance obtained from the allantoic liquid does not act as an acid, the name which it now bears was given to it.[3]

Wöhler afterwards noticed the existence of the same substance in the urine of the sucking calf,[4] and it also occurs in the urine of dogs kept on a fatty diet[5] or after administration of uric acid.[6] It is likewise found in urine in some cases of disease of the respiratory organs;[7] it occurs also after doses of tannic acid have been given, and it exists not unfrequently in the normal fluid.[8] It has also been noticed in the urine of the new-born child, and in small quantities in the case of childbirth.

Schulze and Barbieri have also found allantoïn in the young leaves of the plane-tree (*Platanus orientalis*).[9]

Allantoïn is formed artificially not only by oxidizing uric acid with lead dioxide, but also by acting on the same substance with (1) manganese dioxide,[10] (2) alcoholic solution of potassium ferricyanide,[11] (3) permanganate solution,[12] and (4) ozone:[13]

$$C_5H_4N_4O_3 + H_2O + O = C_4H_6N_4O_3 + CO_2.$$

It is also obtained by the action of nitrous acid on dialuric

[1] *Ann. Chim.* xxxiii. 269.
[2] *Ann. Chim. Phys.* xvii. 301.
[3] *Ann. Chem. Pharm.* xxvi 244.
[4] *Ib.* lxx. 229.
[5] Meissner and Jolly, *Zeitsch. Chem.* 1865, 230.
[6] Salkowski, *Ber. Deutsch. Chem. Ges.* ix. 721.
[7] Frerichs and Städeler, *Jahresb.* 1854, 714.
[8] Salkowski, *Ber. Deutsch. Chem. Ges.* xi. 500.
[9] *Journ. Prakt. Chem.* [2], xxv. 145.
[10] Wheeler, *Zeitsch. Chem.* 1866, 746.
[11] Schlieper, *Ann. Chem. Pharm.* lxvii. 219.
[12] Neubauer, *ib.* xcix. 217; Claus, *Ber. Deutsch. Chem. Ges.* vii. 227.
[13] Gorup-Besanez, *Ann. Chem. Pharm.* cx. 94.

acid,[1] and may be prepared synthetically by heating 1 part of glyoxylic acid with 2 parts of urea for 10 hours:[2]

$$\begin{array}{l} CH(OH)_2 \\ | \\ CO.OH \end{array} + 2\,\begin{array}{l} NH_2 \\ / \\ CO \\ \backslash \\ NH_2 \end{array} = \begin{array}{l} HN{-}CH{-}NH \\ / \quad | \quad \backslash \\ CO \quad | \quad CO \\ \backslash \quad | \quad / \\ HN{-}CO\;\; NH_2 \end{array} + 3H_2O.$$

Allantoïn crystallizes in monoclinic prisms, which, seen under the microscope, exhibit the appearance shown in Fig. 118. These crystals are difficultly soluble in cold water, but dissolve more readily in hot water and in alcohol. It has a neutral reaction, combines with metallic oxides,[3] and yields with mercuric

Fig. 118.

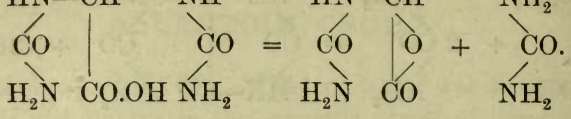
nitrate a white insoluble precipitate similar to that obtained with urea. On this acccunt Liebig's method for the determination of urea cannot be employed in presence of allantoïn.

When allantoïn is heated with concentrated hydriodic acid, it decomposes into urea and glycolyl urea (p. 96).[4]

*Allantoic Acid*, $C_4H_8N_4O_4$, is formed as a difficultly soluble crystalline powder when a solution of allantoïn in caustic potash is allowed to stand for some days. This is a monobasic

[1] Gibbs, *Ann. Chem. Pharm.* Suppl. vii. 337.
[2] Grimaux, *Ann. Chim. Phys.* [5], xi. 389.
[3] Limpricht, *Ann. Chem. Pharm.* lxxxviii. 94.
[4] Schlieper, *Ann. Chem. Pharm.* lxvii. 231; Mulder, *ib.* clix. 362.

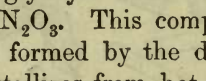
acid, forming crystalline salts.[1] When heated with water it decomposes into urea and allanturic acid (Ponomarew):



*Allanturic Acid*, $C_3H_4N_2O_3$. This was first obtained by Pelouze by oxidizing uric acid and allantoïn.[2] A similar body was afterwards obtained by Schlieper as a by-product in the preparation of allantoïn, and to this he gave the name of *lantanuric acid*, and on boiling alloxanic acid with water he noticed that, together with other products, a deliquescent acid is formed which he described as diffluan.[3] According to Baeyer these bodies are identical, and must be regarded as anhydrides of urea and glyoxylic acid.[4] The formation of allanturic acid from allantoic acid shows that the former substance is the anhydride of carbamine-diglyoxylic acid, a substance which does not appear to exist in the free state.

Allanturic acid is a gum-like deliquescent mass, which when boiled with caustic potash decomposes into ammonia, carbon dioxide, acetic acid, and oxalic acid, or the products of decomposition of uric acid or glyoxylic acid.[5]

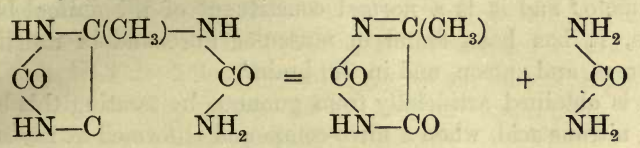
*Glyoxyl-Urea*, $C_3H_4N_2O_3$. This compound is isomeric with allanturic acid, and is formed by the decomposition of oxonic acid (p. 297). It crystallizes from hot water in thick needles, and is a monobasic acid,[6] probably possessing the following constitution:



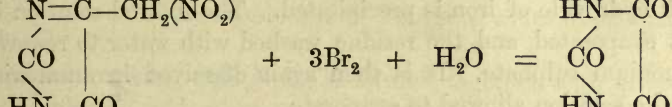
*Glyco-uril*, $C_4H_6N_4O_2$, is formed by the action of sodium amalgam on a hot solution of allantoïn. It crystallizes in small octohedrons or pointed needles, which are difficultly soluble in water.[7] On boiling with dilute sulphuric acid it decomposes into urea and glycolyl urea.[8]

[1] Ponomarew, *Ber. Deutsch. Chem. Ges.* xi. 2155.
[2] Gerhardt, *Traité. Chim. Org.* i. 528.
[3] *Ann. Chem. Pharm.* lvi. 1.
[4] *Neu. Hanwörterb.* i. 288.
[5] Medicus, *Ber. Deutsch. Chem. Ges.* x. 544.
[6] Medicus, *Ann. Chem. Pharm.* clxxv. 234.
[7] Rheineck, *ib.* cxxxiv. 219.
[8] Baeyer, *ib.* cxxxvi. 276.

*Pyruvil*, $C_5H_8N_4O_3$, is isomeric with methyl-allantoïn, and is formed when pyroracemic acid is heated with urea. It crystallizes from hot water in rhombic tables, and when boiled with concentrated hydrochloric acid it is converted into *pyruvinureïde*, $C_4H_4N_2O_2$:



Pyruvil is a crystalline powder somewhat soluble in boiling water. Nitric acid converts it into *nitro-pyruvinureïde*, $C_4H_3(NO_2)N_2O_2$, a body crystallizing from hot water in glistening yellow scales, and dissolving in alkalis with a yellow colour. This latter is a dibasic acid, and is decomposed by boiling with bromine water into parabanic acid and brompicrin :[1]



$$CBr_3NO_2 + 3HBr.$$

## XANTHINE, $C_4H_4N_4O_2$.
## SARCINE, $C_5H_4N_4O$.
## GUANINE, $C_5H_5N_5O$.

682 These three basic compounds, which occur in the animal organism, stand in close relation to uric acid. The two first are formed from this acid by the action of sodium amalgam and water,[2] and guanine is xanthine in which one atom of oxygen is replaced by the imido-group NH, and therefore it is converted into this latter body by the action of nitrous acid.

*Xanthine*, $C_5H_4N_4O_2$, was discovered by Marcet in 1819 as forming the chief constituent of certain rare forms of urinary calculus, and termed by him xanthic oxide, because on evaporation with nitric acid a yellow residue is left (*ξάνθος*, yellow).

[1] Grimaux, *Ann. Chim. Phys.* [5], xi. 373.
[2] Rheineck, *Ann. Chem. Pharm.* cxxxi. 121.
[3] *Essay on the Chemical History and Medical Treatment of Calculous Diseases.*

Its composition was first determined by Liebig and Wöhler, who studied the properties of the body more exactly,[1] whilst Gmelin gave it the name it now bears.[2] It is also always found in small quantity in urine, and during the use of sulphur baths it appears in larger quantity.[3] It also occurs in yeast, frequently in guano,[4] and it is a normal constituent of the animal body. Thus, it has been found in muscular fibre and in the liver, pancreas, and spleen, and in the brain.[5]

It is obtained artificially from guanine by treating this body with nitrous acid, when a nitro-compound is formed at the same time, and this, on reduction with ferrous sulphate and ammonia, yields xanthine.[6] In order to prepare it, potassium nitrate is added to a boiling nitric acid solution of guanine until red nitrous vapours are evolved in considerable quantity, when the solution is diluted with a large quantity of water; the yellow precipitate thus formed is washed and dissolved in boiling ammonia, a solution of ferrous sulphate being then added until black hydroxide of iron is precipitated. The filtered solution is next evaporated, and the residue washed with water to remove ammonium sulphate. It is then again dissolved in ammonia, and the solution allowed to evaporate.

Xanthine is a granular white powder, consisting of microscopic crystals which when pressed possess a waxy lustre. It is deposited from aqueous solution on evaporation as a skin or in scales. It is very difficultly soluble in cold, but more readily soluble in boiling water. The determinations of its solubility vary considerably. According to Almén, it requires from 1336 to 1498 parts of boiling water and about 14,000 parts of cold water for solution.[7] It is insoluble in alcohol, dissolves in ammonia more readily than does uric acid, and is still more readily soluble in caustic potash. Acids, even carbon dioxide, precipitate it from this solution. When xanthine is heated a small portion sublimes; the larger portion, however, carbonizes with formation of ammonium carbonate, cyanogen, and hydrocyanic acid.

Xanthine acts at the same time as a weak acid and a weak base. It dissolves in warm ammonia, and on cooling fine stellated needles of the ammonium compound separate out, but the solution when evaporated loses the whole of its ammonia. Xanthine

[1] *Pogg. Ann.* xli. 393.
[2] *Handb. Org. Chem.* ii. 514.
[3] Dürr, *Ann. Chem. Pharm.* cxxxiv. 45.
[4] Strecker, *ib.* cxviii. 152; Phipson, *Chem. News*, vi. 16.
[5] Scherer, *Ann. Chem. Pharm.* cxii. 257.
[6] Strecker, *ib.* cviii. 141, cxviii. 166.
[7] *Jahresb.* 1862, 534.

separated out by acetic acid is more easily soluble than that obtained by evaporation (Strecker, Scherer). When xanthine is boiled with baryta-water, the difficultly soluble compound $C_5H_4N_4O_2Ba(OH)_2$ separates out.

*Xanthine Sulphate*, $C_5H_4N_4O_2,SO_4H_2+H_2O$, crystallizes in microscopic, glistening, rhombic tables, which when washed with water lose the whole of their acid. *Xanthine hydrochlorate*, $C_5H_4N_4O_2,HCl$, is difficultly soluble in water, and is deposited in glistening scales aggregated in nodular concretions. The *nitrate* forms fine yellow crystals.

When xanthine is evaporated with nitric acid, and caustic potash added to the yellow residue, this becomes of a yellowish-red colour, which on warming turns to a violet-red. If a small quantity of xanthine is brought on to a watch-glass with a mixture of bleaching powder and caustic soda, the edges of the liquid become covered with a dark-green scum which soon becomes brown and disappears. The soluble salts of mercury precipitate an aqueous solution of xanthine even when greatly diluted.

*Pseudoxanthine*, $C_5H_4N_4O_2$, is formed, together with glycocoll and hydurilic acid, when uric acid is heated with sulphuric acid to a temperature of 110°—130°. It is a white powder, slightly soluble in water, but easily soluble in caustic potash. When it is evaporated with nitric acid, it leaves a lemon-yellow residue which is coloured yellowish-red by caustic alkalis. With nitric acid or hydrochloric acid it does not form crystalline compounds.[1]

683 *Sarcine*, $C_5H_4N_4O$. A substance resembling xanthine was discovered by Scherer in splenic pulp and in the muscles of the heart, and to this he gave the name of hypoxanthine, as it contains one atom of oxygen less than xanthine. A body termed xanthoglobuline, which the same chemist discovered in the liver and pancreas, appeared to be different from this substance, whilst Strecker found a compound having the same composition as hypoxanthine in muscular fibre, and as it did not agree in its properties with this body he distinguished it as sarcine. Scherer then showed that the bodies which he had obtained were identical with this latter, and that the differences which were noted were due to the fact that they were mixed with more or less xanthine or guanine.[2]

[1] Schultzen and Filehne, *Ber. Deutsch. Chem. Ges.* i. 150.

[2] Scherer, *Ann. Chem. Pharm.* lxxiii. 328 cvii. 314, cxii. 257; Strecker, *ib.* cii. 204, cviii. 129.

Sarcine almost always occurs together with xanthine, and is also found in the spinal marrow, and in the blood after death, but not in blood when flowing through the blood-vessels; it does not occur in urine.

In order to prepare this compound, extract of meat is dissolved in fifteen times its weight of water, the solution precipitated with acetate of lead, the filtrate then freed from lead by sulphuretted hydrogen, and evaporated to one-fourth of its original volume. Ammonia is next added and silver nitrate, the precipitate washed with ammoniacal water, and dissolved in the smallest possible quantity of nitric acid of specific gravity 1·1. On cooling, sarcine-silver-nitrate crystallizes out, this requiring 5,000 parts of the cold acid for solution. The precipitate is then freed from nitric acid by washing with ammoniacal silver solution, the residue suspended in water and decomposed by sulphuretted hydrogen. The filtrate, on evaporation, yields absolutely pure sarcine, of which the extract of meat contains about 0·6 per cent., whilst ox-muscle contains from 0·0161 to 0·0277 per cent. The filtrate from the sarcine-silver-nitrate gives on addition of ammonia a precipitate of xanthine-silver-oxide, and hence this method serves for the quantitative determination of sarcine and xanthine in meat. The preparation of creatine may also be carried out in the same material.[1]

Sarcine is a crystalline powder, dissolving in 300 parts of cold and 78 parts of boiling water, and being less soluble in alcohol. Fuming nitric acid converts it into xanthine and a nitro-compound. It has a neutral reaction, and combines with acids, bases, and salts.

*Hydrochlorate of Sarcine*, $C_5H_4N_4O,HCl + H_2O$, crystallizes in needles or prisms, and is readily decomposed by water. The *nitrate* forms thick prisms, which become opaque when moistened.

The *barium salt*, $C_5H_4N_4O,Ba(OH)_2$, or $C_5H_2BaN_4O + 2H_2O$, is obtained by dissolving sarcine in dilute, and afterwards adding an excess of cold saturated, baryta-water, when the salt is deposited in transparent crystals.

When sarcine solution is precipitated with ammoniacal silver nitrate, a gelatinous precipitate, having the composition $C_5H_3AgN_4O + H_2O$ is deposited, whilst with silver nitrate alone flocks of $C_5H_4N_4O,AgNO_3$ are formed, which dissolve in dilute nitric acid, and on cooling the salt is deposited in microscopic needles.

[1] Neubauer, *Fresenius' Zeitsch.* vi. 33.

684 *Carnine*, $C_7H_8N_4O_3$, has hitherto only been found in Liebig's extract of meat,[1] and in order to prepare it this is dissolved in 6 to 7 parts of water, precipitated by baryta-water, and acetate of lead added to the filtrate, when a precipitate is formed which contains the lead compound of carnine. This is then dissolved by boiling repeatedly with water, and the solution decomposed by passing sulphuretted hydrogen through it. The filtrate is then concentrated, and a strong solution of silver nitrate added, when a flocculent precipitate, having the composition $(C_7H_8N_4O_3)_2,AgNO_3$, is formed. This is washed with dilute ammonia to remove nitric acid. The precipitate is, lastly, suspended in water, and decomposed by sulphuretted hydrogen.

Carnine is a crystalline powder, difficultly soluble in water; it unites with hydrochloric acid to form the salt $C_7H_8N_4O_3 + 3HCl$, crystallizing in glistening needles. Bromine-water or warm nitric acid converts carnine into sarcine. Extract of meat contains about 1 per cent. of carnine, and it is from this that the sarcine is probably formed.

685 *Guanine*, or *Imidoxanthine*, $C_5H_5N_5O$. This body was discovered by Unger in various samples of guano, being contained in largest quantity in that from Peru.[2] It is also found in the excrement of the spider,[3] in the pancreas of the horse,[4] and in the scales of the bleak,[5] and it occurs as a deposit in the knee-joints of swine suffering from the disease known as Guanine-gout (Virchow).

It is produced, together with xanthine, sarcine, and other bodies, when yeast is allowed to stand at a temperature of 35° in contact with water.[6]

In order to prepare it, Peruvian guano is suspended in water, milk of lime gradually added, and the whole boiled. The brown solution is then squeezed through a cloth, and the process repeated until the liquid is no longer coloured. The residue, which contains uric acid and guanine, is then boiled with solution of sodium carbonate, until the solution thus obtained no longer yields a precipitate with hydrochloric acid. It is then treated with sodium acetate, and hydrochloric acid added to strongly acid reaction, and the precipitate boiled with dilute hydrochloric acid. Hydrochlorate of guanine crystallizes out on cooling, but this still contains uric acid, and to remove

[1] Weidel, *Ann. Chem. Pharm.* clviii. 353.
[2] *Ann. Chem. Pharm.* lix. 58.
[3] Gorup-Besanez and Will, *ib.* lxix. 117.
[4] Scherer, *ib.* cxii. 276.
[5] Barreswill, *Compt. Rend.* liii. 246.
[6] Schutzenberger, *Bull. Soc. Chim.* vii. 192.

this it must be boiled with dilute ammonia, and the residual guanine dissolved in strong, boiling nitric acid. On cooling, nitrate of guanine separates out, and this may be decomposed by ammonia.[1]

Guanine is an amorphous powder, insoluble in water. It dissolves, however, in an excess of concentrated ammonia,—a reaction which distinguishes it from xanthine and sarcine. Its salts also yield with potassium chromate an orange-red, crystalline precipitate, and potassium ferricyanide gives a reddish-brown, crystalline precipitate, whilst a saturated solution of picric acid gives an orange-yellow, silky, insoluble picrate.[2] When guanine is evaporated with fuming nitric acid, a glistening yellow residue remains, and this, on the addition of caustic soda, becomes first red, and then, on heating, purple.

When guanine is heated with hydrochloric acid and potassium chlorate, it is oxidized to carbon dioxide, guanidine, and parabanic acid (Strecker). It is a diacid base, but also forms metallic salts, and combines with salts.

*Guanine Hydrochlorate*, $C_5H_5N_5O,(HCl)_2$, is formed when hydrochloric acid gas is passed at a low temperature over guanine, when the mass swells up. By dissolving guanine in hot hydrochloric acid, the monacid salt having the formula $C_5H_5N_5O,HCl + 2H_2O$ is obtained, crystallizing in needles which lose their water at 100° and their acid at 200°. Guanine hydrochlorate forms double salts with various metallic chlorides. The platinichloride, $[C_5H_5N_5O,HCl]_2+PtCl_4+2H_2O$, crystallizes from water in orange-yellow prisms.

*Guanine Sulphate*, $(C_5H_5N_5O)_2,H_2SO_4$, crystallizes in long needles, but is decomposed by prolonged washing with water.

*Guanine Nitrate*, $C_5H_5N_5O,(HNO_3)_2+2H_2O$, is formed by dissolving guanine in hot nitric acid of specific gravity 1·25. It crystallizes in short prisms. From more dilute acid, a salt, having the composition $2(C_5H_5N_5O,HNO_3)+3H_2O$, crystallizes in long, hair-like, foliated needles.

Guanine also forms, with oxalic acid and tartaric acid, crystalline salts (Unger), but it does not combine with formic or acetic acid, and does not dissolve in lactic acid or citric acid.[3]

Guanine dissolves readily in caustic soda solution, and on the addition of alcohol indistinctly formed scales, having the com-

[1] Strecker, *Ann. Chem. Pharm.* cxviii. 152.
[2] Capranica, *Hoppe-Seyler's Zeitsch. Phys. Chem.* iv. 233.
[3] Neubauer and Kerner, *Ann. Chem. Pharm.* ci. 318.

position $C_5H_5N_5O,(NaOH)_2+5H_2O$, separate out, and these are decomposed by water and by carbon dioxide (Unger). When guanine is dissolved in boiling baryta-water, needles separate out on cooling which, when dried over sulphuric acid, lose their water and have the composition $C_5H_3BaN_5O$ (Strecker).

If a concentrated aqueous solution of corrosive sublimate be added to a hydrochloric acid solution of guanine, a crystalline precipitate, having the composition $2(C_5H_5N_5O,HgCl_2)+5H_2O$, is formed. A hot alcoholic solution of sublimate gives, on the other hand, a heavy, crystalline powder, consisting of microscopic prisms, having the composition $2(C_5H_5N_5O,HCl)HgCl_2+H_2O$ (Neubauer and Kerner).

Silver nitrate gives a flocculent precipitate in a solution of nitrate of guanine, and this dissolves in strong boiling nitric acid, and on cooling deposits in fine, needle-shaped crystals, having the formula $C_5H_5N_5O,AgNO_3$ (Strecker).

## THEOBROMINE, $C_7H_8N_4O_2$.

## CAFFEÏNE, $C_8H_{10}N_4O_2$.

686 These two compounds, which only occur in the vegetable kingdom, and which were formerly classed amongst the alkaloids, are now known to exhibit chemical analogies with uric acid and similar bodies occurring in the animal organism.

*Theobromine*, $C_7H_8N_4O_2$. This body was discovered by Woskresensky in cocao-beans, the fruit of *Theobroma cacao*,[1] from which cocao and chocolate are prepared. It also occurs in the rind,[2] and, as it appears, in small quantity together with caffeïne in the young leaves of Himalaya tea.[3] In order to extract it the powdered beans, which contain about 0·5 per cent., are boiled with water, and lead acetate added to the solution until no further precipitate is formed. The filtrate is then freed from lead by sulphuretted hydrogen, and evaporated to dryness. The residue is boiled with alcohol, and, on cooling, theobromine crystallizes out, and is then purified by recrystallization or by sublimation.

Strecker found that when silver nitrate is added to an ammoniacal solution of xanthine, an amorphous precipitate of

[1] *Ann. Chem. Pharm.* xli. 125.
[2] Bley, *Pharm. Central.* 1842, 303.
[3] Zöller, *Ann. Chem. Pharm.* clviii. 180.

xanthine-silver, $C_5H_2Ag_2N_4O_2$, is formed, and this, when heated with methyl iodide is converted into dimethyl xanthine, $C_5H_2(CH_3)_2N_4O_2$. He considered that this body was isomeric with theobromine,[1] but E. Fischer has shown that the bodies are identical. In order to prepare theobromine from xanthine, a molecule of the latter is dissolved in a solution of two molecules of caustic soda and the boiling solution precipitated with acetate of lead, when lead xanthine, $C_5H_2PbN_4O_2$, is thrown down as a crystalline precipitate, which, when heated with methyl iodide to 100°, is converted into theobromine.[2]

Theobromine is slightly soluble in water, and forms microscopic crystals which sublime to a snow-like mass at 290°—295°.[3] It possesses a bitter taste, which, however, only becomes perceptible after a time. It combines with acids to form unstable salts, which resemble those of caffeïne. When dissolved in ammonia, and silver nitrate added and the mixture boiled, silver-theobromine, $C_7H_7AgN_4O_2$, is deposited as a white precipitate.

On oxidation with chromic acid, theobromine yields monomethylparabanic acid,[4] whilst aqueous chlorine converts it into monomethyl urea and monomethyl alloxan,[5] and by hydrochloric acid and chlorate of potash it is oxidized to dimethyl-alloxantin, $C_8H_4(CH_3)_2N_4O_8 + 4H_2O$ (Maly and Hinteregger).

687 *Caffeïne*, or *Methyl Theobromine*, $C_8H_{10}N_4O_2$. The bitter ingredient of coffee was not obtained in the pure state till the year 1821,[6] when it was prepared almost simultaneously by Runge,[7] Pelletier and Caventon,[8] and Robiquet.[9] In 1827 Oudry discovered the bitter crystalline principle contained in tea, to which he gave the name of *theïne*;[10] and Berzelius suggested that this compound would be found to be identical with that obtained from coffee, and his supposition was proved to be correct by the investigations of Jobst[11] and Mulder.[12] A body termed guaranine by Martius was afterwards shown by himself,[13] and by Bertemont and Dechastelus,[14] to be caffeïne.

The exact composition of this body was ascertained by Pfaff

[1] *Ann. Chem. Pharm.* cxviii. 174.
[2] *Ber. Deut. Chem. Ges.* xv. 453.
[3] Keller, *Ann. Chem. Pharm.* xcii. 71.
[4] Maly and Hinteregger, *Monats. Chem.* 1881, 87.
[5] E. Fischer, *Ber. Deutsch. Chem. Ges.* xv. 62.
[6] *Gmelin's Handbook*, xiii. 224.
[7] *Materialen zur Physiologie*; see also Giske, *Schweigg. Journ.* xxxi. 208.
[8] *Journ. Pharm.* [2], xii. 229.
[9] *Dict. Technol.*
[10] *Nouv. Bibl. Med.* March, 1827.
[11] *Ann. Chem. Pharm.* xxv. 63.
[12] *Journ. Prakt. Chem.* xv. 280.
[13] *Ann. Chem. Pharm.* xxxvi. 93.
[14] *Ib.* xxxvi. 90.

and Liebig,[1] but Strecker was the first to obtain caffeïne artificially. For this purpose he heated silver-theobromine with methyl iodide, proving that this body is methyl-theobromine.[2]

Coffee-beans contain 0·5 to 2·2 per cent. of caffeïne. It is found in the seed-cover as well as in the leaves[3] of the coffee-plant, which contain in the dry state about 1·26 per cent. (Stenhouse). The percentage of caffeïne in tea varies usually between 1·5 and 2·5 per cent., but in some cases it rises to above 3·2 per cent. Guarana or uarana, termed Brazilian chocolate, a material largely used in South America, is the roasted pulp of the fruit of *Paullinia sorbilis*. This substance occurs in commerce in reddish-brown cylinders or balls, and serves as an article of diet as well as a medicine. It contains 1·5 to 5 per cent. of the base. Caffeïne is also contained in Paraguay tea or "yerba mate," a substance obtained from the leaves and small twigs of the *Ilex Paraguayensis*, and which contains 0·2 to 1·6.[4] It is also found in Kola-nuts, the fruit of the *Sterculia acuminata*, used in Central Africa as a food, and this contains about 2 per cent. of caffeïne.[5]

In order to prepare caffeïne, tea-dust is employed. This is boiled with water, acetate of lead added to the solution until no further precipitate occurs, in order to get rid of tannic acid and other bodies, the filtrate freed from lead by sulphuretted hydrogen, and the whole evaporated to the point of crystallization. The impure base is then recrystallized from alcohol, benzene, or chloroform. It forms long, silky, elastic needles, which when crystallized from water contain one molecule of this substance, which is given off at 100°. It dissolves in about 90 parts of cold water, and easily in boiling water. It is less soluble in alcohol, and still more difficultly soluble in ether. On the other hand, it dissolves readily in chloroform and benzene. It possesses a slightly bitter taste, melts at 234°—235°, and sublimes without decomposition.

In order to determine the amount of caffeïne in tea or coffee, 10 grams of the substance, which must be well dried and powdered, are boiled with water, and the filtrate evaporated to dryness with 2 grams of magnesia and 5 grams of glass powder. The caffeïne is then extracted with a mixture of 1 part of

[1] *Ann. Pharm.* i. 17. [2] *Ann. Chem. Pharm.* cxviii. 170.
[3] Van der Corput, *Gmelin's Handbook*, xiii. 225; Stenhouse, *Ann. Chem. Pharm.* lxxxix. 244.
[4] Stenhouse, *Mem. Chem. Soc* i. 218.
[5] Attfield, *Pharm. Journ. Trans.* [2], vi. 45.

chloroform and 3 parts of ether, and the solution evaporated to dryness.

Caffeïne has a neutral reaction. It is a very weak base, the salts of which are decomposed by water or on warming. As the older literature on the subject contains many contradictions, E. Schmidt has recently investigated the subject anew.[1]

*Hydrochloride of Caffeïne*, $C_8H_{10}N_4O_2,HCl + 2H_2O$, separates from a solution of the base in concentrated hydrochloric acid in rhombic prisms, which lose water and acid on exposure to air, and on heating to 100° leave pure caffeïne. If hydrochloric acid gas be passed over caffeïne, it absorbs two molecules of the gas, which are gradually given off again on exposure under the exsiccator.[2] The platinichloride, $(C_8H_{10}N_4O_2,HCl)_2PtCl_4$, is difficultly soluble in water and alcohol, and separates from hot water in small yellow crystals. When concentrated solutions of auric chloride and caffeïne hydrochloride are mixed, the solution solidifies to a splendid, lemon-yellow, crystalline mass, which is deposited from alcoholic solution in long, orange-yellow needles, having the composition $C_8H_{10}N_4O_2,HCl(AuCl_3)$.[3]

*Caffeïne Sulphate*, $C_8H_{10}N_4O_2,SO_4H_2$, separates in glistening needles from a hot alcoholic caffeïne solution to which sulphuric acid has been added.

*Caffeïne Acetate*, $C_8H_{10}N_4O_2,(C_2H_4O_2)_2$, forms needle-shaped crystals, which lose acid on exposure to air, and more readily at a high temperature. Butyric and valeric acids also form compounds with caffeïne, but these contain only one molecule of the acid.

The material occurring in commerce termed citrate of caffeïne is not a salt, but the base itself.

Caffeïne is poisonous. It produces increased action of the heart and nervous irritability: 0·3 gram of the body given to a rabbit produces symptoms of poisoning, whilst 0·37 to 0.5 gram killed both a rabbit and a cat in the space of half an hour to two hours. In the process of roasting the coffee does not lose any perceptible amount of caffeïne, and its physiological action depends to a certain extent upon the presence of this base, but not entirely upon this, as it has been shown that tea has a different action upon the nerves than coffee, and in the latter case the aromatic oil which is formed in the process of roasting plays

[1] *Ber. Deutsch. Chem. Ges.* xiv. 814.
[2] Mulder, *Pogg. Ann.* xliii. 161.
[3] Nicholson, *Ann. Chem. Pharm.* lxii. 71.

an important part,[1] whilst in the case of tea the large quantity of tannic acid which it contains modifies the action of the caffeïne.

Coffee and tea, and probably other dietetics which contain caffeïne, stimulate nervous action and diminish metabolism, and for this reason the desire for sleep and nourishment after the use of such beverages becomes less. This fact appears to have been long known to the Arabs, who accordingly use coffee in their feasts and nocturnal religious ceremonies. The Arabic word for coffee-bean is *Bounne*, but the beverage is termed *Kahwa*, derived from *Ikha*, signifying distaste (for food or sleep).[2]

688 By the action of concentrated nitric acid on caffeïne, Stenhouse obtained a compound having the composition $C_5H_6N_2O_3$, to which he gave the name of *nitro-theïne*.[3] Rochleder then found that this body is also obtained when caffeïne is treated with chlorine in presence of water, whilst, together with this, amalic acid, $C_{12}H_{12}N_4O_7$, methylamine, and cyanogen chloride are formed. Stenhouse's compound was termed *cholestrophane*,[4] owing to its similarity to the body cholesterine contained in the bile. Strecker then showed that this compound is dimethyl-parabanic acid, and that amalic acid is tetramethyl-alloxantin.[5] He also proved that when caffeïne is heated with baryta-water, carbon dioxide and caffeïdine, $C_7H_{12}N_4O$, are formed.[6] This latter body is a strong base, which, when further heated with alkalis, yields ammonia, methylamine, sarcosine (methylamido-acetic acid), formic acid, and carbon dioxide :[7]

$$C_7H_{12}N_4O + 5H_2O = NH_3 + 2CH_3.NH_2 + C_3H_7NO_2 + CH_2O_2 + CO_2.$$

These reactions show that caffeïne contains the methyl group three times, and that its constitution must be very similar to that of uric acid. The investigations of E. Fischer have substantiated this in a remarkable manner. He has shown that caffeïne, when acted upon by oxidizing agents, is converted first into dimethyl-alloxan and monomethyl-urea, whilst uric acid thus treated gives, as has been stated, alloxan and urea.

[1] Lehmann, *Ann. Chem. Pharm.* lxxxvii. 207 and 275.
[2] De Sacy, *Chrestomatie Arabe.*
[3] *Mem. Chem. Soc.* i. 219,239. Rochleder, *Ann. Chem. Pharm.* lxxiii. 56.
[4] *Ann. Chem. Pharm.* cxviii. 174.
[5] *Ib.* cxxiii. 360.
[6] Schultzen, *Zeitsch. Chem.* 1867, 614 ; Rosengarten and Strecker, *Ann. Chem. Pharm.* clvii. 1.

Fischer has moreover prepared a series of other derivatives, the relations of which enable us to explain the constitution of caffeïne in a simple way.[1]

*Chlorcaffeïne*, $C_8H_9ClN_4O_2$, separates from aqueous solution in a voluminous crystalline mass, and crystallizes from water in needles (Rochleder).

*Bromcaffeïne*, $C_8H_9BrN_4O_2$, was first obtained by Schultzen,[2] and then investigated by Fischer. When 1 part of caffeïne is brought in contact with 5 parts of bromine, a dark-red addition-product is obtained, which, when heated for twelve hours and the excess of bromine distilled off and the residue heated to 150°, is converted into bromcaffeïne. In order to purify this product it is treated with aqueous sulphurous acid, dissolved in concentrated hydrochloric acid, and precipitated with water. It closely resembles the chlorine compound. It melts at 206°, sublimes when gently heated, and is difficultly soluble in water and alcohol. When heated with alcoholic ammonia, *amidocaffeïne*, $C_8H_9(NH_2)N_4O$, is formed, a body crystallizing in fine needles, and which can be distilled without decomposition. It is easily soluble in strong hydrochloric acid, and is precipitated again by water.

When bromcaffeïne is boiled with alcohol and caustic potash, *ethoxycaffeïne*, $C_8H_9(OC_2H_5)N_4O_2$, is formed, a body which yields colourless crystals, melting at 140°, difficultly soluble in water, but dissolving readily in alcohol.

689 *Hydroxycaffeïne*, $C_8H_9(OH)N_4O_2$, is formed, together with ethyl chloride, when a hydrochloric acid solution of the last-named compound is warmed. It crystallizes from hot water in white foliated needles, which melt at about 350°. It is an acid yielding a crystalline potassium salt. With bromine it forms an addition-product which is very unstable, and is converted by alcohol into *diethoxyhydroxycaffeïne*, $C_8H_9(OH)N_4O_2(OC_2H_5)_2$. This crystallizes from hot alcohol in fine prisms, which melt without decomposition at about 200°, and it is also easily formed when hydroxycaffeïne is suspended in alcohol and bromine added. On evaporating it with strong hydrochloric acid, *apocaffeïne*, $C_7H_7N_3O_5$, is formed, a body crystallizing in opaque prisms which melt at 147°—148°. On boiling with water it is converted, with evolution of carbon dioxide, into *hypocaffeïne*, $C_6H_7N_3O_3$, which, on cooling, is deposited in large crystals

[1] *Ber. Deutsch. Chem. Ges.* xiv. 637 and 1905, xv. 30.
[2] *Zeitsch. Chem.* 1867, 614.

melting at 181°. It is an acid, and a very stable body, not acted upon by oxidizing or reducing agents, but easily attacked by alkalis.

*Caffolin*, $C_5H_9N_3O_2$, is formed when hypocaffeïne is warmed together with baryta-water or acetate of lead. It crystallizes from hot water in long white prisms, which melt at 194°—196°, On oxidation with alkaline ferricyanide of potassium solution it yields methyl-urea and methyloxamic acid :

$$C_5H_9N_3O_2 + H_2O + O = C_2H_6N_2O + C_3H_5NO_3.$$

An alkaline permanganate solution oxidizes it to ammonia, carbon dioxide, and dimethyloxamide.

*Caffuric Acid*, $C_6H_9N_3O_4$, is formed as a by-product in the preparation of hypocaffeïne. It is easily soluble in water, and crystallizes from hot alcohol in splendid glistening prisms, which effloresce on exposure. It is a monobasic acid, and on heating with lead acetate is converted into mesoxalic acid, methylamine, and methyl-urea :

$$C_6H_9N_3O_4 + 3H_2O = C_3H_2O_6 + CH_5N + C_2H_6N_2O.$$

On reduction it is converted into *hydrocaffuric acid*, $C_6H_9N_3O_3$, crystallizing in needles, and melting at 245°.

690 *Amalic Acid* or *Tetramethyl-alloxantin*, $C_8(CH_3)_4N_4O_7 + H_2O$. It has already been stated that Rochleder, by acting with chlorine upon caffeïne in presence of water, obtained the so-called amalic acid, this name being derived from ἄμαλις, weak, "to indicate the weak acid nature of this body, as well as the slight affinity with which its elements are united." According to Fischer it is best obtained by the following process. Fifteen parts of caffeïne are dissolved in 20 parts of hydrochloric acid of specific gravity 1·19, and 45 parts of water warmed to 50°. To this 7 parts of potassium chlorate are gradually added, till a clear solution is formed. This then contains methyl-urea, dimethyl-alloxan, apocaffeïne, and caffeic acid (Maly and Hinteregger). On evaporation, the dimethyl-alloxan is converted into tetramethyl-alloxan. This is more readily obtained if the hydrochloric acid solution, diluted with an equal volume of water, be treated with as much sulphur dioxide as is sufficient to neutralize the free chlorine, and then saturated with sulphuretted hydrogen. The precipitate is filtered off and boiled with water, and on cooling amalic acid separates out in crystals, whilst methyl-urea can be prepared from the first filtrate.

Amalic acid is difficultly soluble in cold water, and also but slightly soluble in hot water, and it forms transparent crystals. In its properties it resembles alloxantin. Sulphuretted hydrogen reduces it to dimethyl dialuric acid, the solution of which brought together with dimethylalloxan again yields amalic acid (Maly and Hinteregger). When brought on to the skin it imparts to it a red colour and a disagreeable smell; it is coloured dark violet by alkalis, and yields with ferrous sulphate and the addition of an alkali, an indigo-blue precipitate. Heated alone it becomes yellow, and afterwards a reddish-brown, and then dissolves in water with a purple-red colour. In the presence of air, water, and ammonia it forms *murexoïn*, a body which, according to Gerhardt, is *tetramethyl-murexide*, $C_8(CH_3)_4N_5O_6(NH_4)$. This crystallizes from hot water in scarlet-red, four-sided prisms, of which two of the surfaces reflect light with a golden lustre.[1]

*Test for Caffeïne.* The formation of the last-named body has been employed for the detection of caffeïne and theobromine. The substance is dissolved in chlorine water, and evaporated to dryness, when a purple-red residue remains, and this on heating and addition of ammonia becomes red again. In this way the presence of caffeïne in a single coffee-berry can be detected.[2]

When amalic acid is carefully oxidized with nitric acid; dimethylalloxan, $C_4(CH_3)_2(OH)_2N_2O_3+H_2O$, is formed, a body crystallizing in thick six-sided tables, and staining the skin red, but not imparting to it a disagreeable smell.[3]

691 *Caffeïdine*, $C_7H_{12}N_4O$, is formed from caffeïne, as has been stated, by loss of carbon dioxide and addition of hydrogen. In order to prepare it, caffeïne is heated with ten times its weight of crystallized barium hydroxide, dissolved in water, and boiled until an evolution of ammonia and methylamine is noticed. The excess of baryta is then thrown down by dilute sulphuric acid and the solution concentrated, when, on standing, *caffeïdine sulphate*, $C_7H_{12}N_4O,SO_4H_2$, separates out in thick needles. The free base which is prepared from the salt is an oily liquid, soluble in water, and having a strongly alkaline reaction, and decomposing on heating. The *hydrochloride*, $C_7H_{12}N_4O,ClH$, crystallizes in needles, and yields a platinichloride which crystallizes from water in large orange-yellow needles, containing

[1] Rochleder, *Ann. Chem. Pharm.* lxxi. 1, lxxiii. 56.
[2] Schwarzenbach, *Jahresb.* 1861, 891; 1864, 730.
[3] Maly and Andreasch, *Monatsh.* iii. 92.

either two or four molecules of water. Caffeïdine unites with ethyl iodide to form the compound $C_7H_{11}(C_2H_5)N_4OIH$, and the *ethyl-caffeïdine* which can be obtained from this is capable of again uniting with ethyl iodide.[1]

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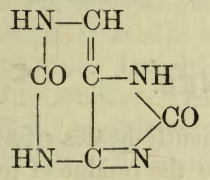
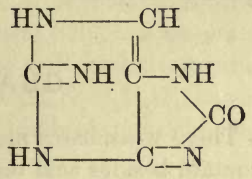
692 Like uric acid, caffeïne contains three atoms of carbon which are directly united with one another, and, like this body, it is a diureïde in which three methyl groups occur. In addition to this, caffeïne contains one atom of hydrogen capable of being replaced by chlorine, bromine, hydroxyl, &c., and lastly its power to form addition-products shows that two of its carbon atoms are connected by double linkages. From these considerations, from the reactions already treated of, and from the fact of its artificial formation from xanthine, the following constitutional formulæ for some of the above-mentioned caffeïne compounds are derived :

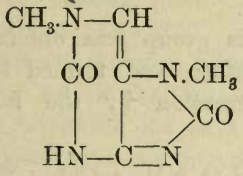
Xanthine.



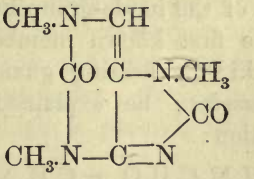
Guanine.



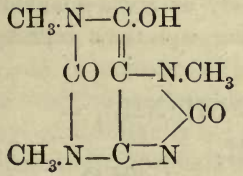
Theobromine.



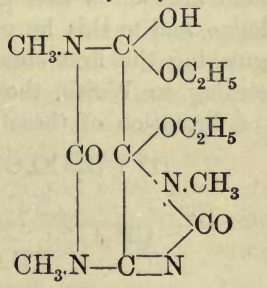
Caffeïne.



Oxycaffeïne.

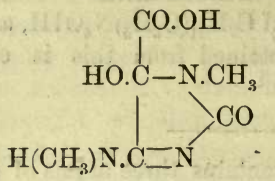


Diaethohydroxycaffeïne.

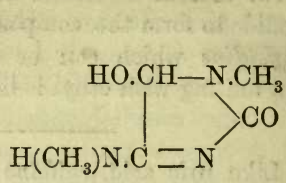


[1] E. Schmidt, *Ber. Deutsch. Chem. Ges.* xiv. 816.

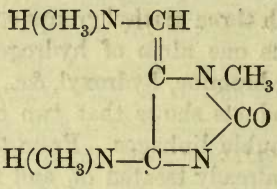
Caffuric Acid.



Caffolin.



Caffeïdine.



As xanthine can be easily obtained from guanine it may prove possible to prepare theobromine and caffeïne, substances which are constituents of several important articles of food, from guano.

## GUANAMINES.

693 These weak bases may conveniently be described here, as they contain besides acid residues also the residue of guanidine, which can be transformed into a urea-residue by the replacement of the imido-group by oxygen.

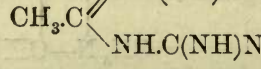
The first known member of this group was obtained by Nencki[1] by heating guanidine acetate, and termed by him *guanamine;* he explained its formation by the following equation:

$$3CH_5N_3.C_2H_4O_2 = C_4H_7N_5 + 2C_2H_4O_2.NH_3 + CO_2 + 2NH_3.$$

He found afterwards that guanidine formate yields the lower homologue, and to this he gave the name of *formo-guanamine,* distinguishing the first obtained body as aceto-guanamine.[2]

According to Weith, the following equations represent the mode of formation of these bases:

(1) $CH_3.CO.OH + 2C(NH)(NH_2)_2 =$



[1] *Ber. Deutsch. Chem. Ges.* vii. 775 [2] *Ib.* 1584.

(2) $CH_3.C\begin{matrix}\diagup N.C(NH)NH_2 \\ \diagdown NH.C(NH)NH_2\end{matrix} = CH_3.C\begin{matrix}\diagup N\,.\,C=NH \\ \diagdown NH.C=NH\end{matrix}\!\!\diagdown NH + NH_3.$

The water which is formed decomposes a part of the guanidine with formation of ammonia and carbon dioxide, whilst the excess of acetic acid forms ammonium acetate.[1]

Nencki afterwards prepared higher homologues of this group. He then distinguished the first member of the series by the name of guanamine simply; whilst aceto-guanamine he termed methylene-guanamine, and to the butyro-guanamine he gave the name of propylene-guanamine.[2] As, however, the higher members of this series differ from the first by the replacement of one atom of hydrogen in the methenyl group by alcohol radicals, these compounds may appropriately be designated, as has been suggested by Henry Watts, by the names guanamine, methyl-guanamine, propyl-guanamine, &c.[3]

*Guanamine*, or *Formo-guanamine*, $C_3H_5N_5$, crystallizes from hot water in rhombic needles, which melt at 350°, and have a faintly alkaline reaction. Its salts crystallize well, and are for the most part readily soluble. The oxalate, $C_3H_5N_5.C_2H_2O_4$, however, is a crystalline precipitate which is insoluble in cold, and but slightly soluble in hot, water.

*Methyl-guanamine*, or *Aceto-guanamine*, $C_4H_7N_5$, is obtained by gradually heating guanidine acetate until the residue boils constantly at 228°—230°. It is kept at this temperature for about fifteen minutes, allowed to cool, and the residue then extracted with a small quantity of hot water. On cooling, the acetate separates out as a jelly, which is pressed, and then decomposed with caustic soda solution.

Methyl-guanamine is only slightly soluble in cold water, but dissolves readily in hot water and in alcohol. It crystallizes from aqueous solution by rapid cooling in mother-of-pearl glistening scales, whilst, when slowly cooled, large rhombic plates or needles are deposited, containing water of crystallization, which they readily lose in contact with air. It is tasteless, has a faintly alkaline reaction, and yields salts which crystallize well.

Methyl-guanamine is not poisonous, and after administration passes unchanged through the animal organism into the urine.

*Guanamine Hydrochloride*, $C_4H_7N_5,HCl + 2H_2O$, crystallizes

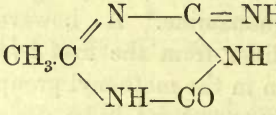
[1] *Ber. Deutsch. Chem. Ges.* ix. 458; Nencki, *ib.* 1013. [2] *Ib.* 228.
[3] *Dict. Chemistry*, Suppl. iii. 901.

in monoclinic prisms or tables. The platinichloride is a yellow crystalline powder, which dissolves readily in water.

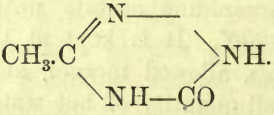
*Guanid*, $C_4H_6N_4O$, is formed by boiling methyl-guanamine with concentrated potash solution:

$$C_4H_7N_5 + H_2O = C_4H_6N_4O + NH_3.$$

It is a chalk-white crystalline powder, practically insoluble in water and alcohol. It dissolves readily, however, in the fixed alkalis, and with mineral acids yields crystalline readily-soluble salts. Its constitution is probably expressed by the following formula:



*Guanamide*, $C_4H_5N_3O_2$, is formed by heating methyl-guanamine with concentrated sulphuric acid. It dissolves readily in water, alkalis, and acids, and crystallizes from hot alcohol in small rhombic needles. Nitric acid oxidizes it to cyanuric acid. When heated with bromine, it yields *tribromguanamide*, $C_4H_2Br_3N_3O_2$, which forms small crystals insoluble in water, and when boiled in contact with this liquid it splits up into cyanuric acid and bromoform.[1] The constitution of guanamide is shown by the following formula:



Nencki and Baudrowski have prepared the following members of the guanamine series.[2]

| | | M.P. |
|---|---|---|
| Propyl-guanamine, | $C_3H_7.C_3H_4N_5$ four-sided tables. | Sublimes without melting. |
| Isopropyl-guanamine, | $(CH_3)_2CH.C_3H_4N_5$ rhombohedrons | — |
| Isobutyl-guanamine, | $(CH_3)_2C_2H_3.C_3H_4N_5$ rhombic needles. | 172°-175° |
| Amyl-guanamine, | $(CH_3)_2C_3H_5.C_3H_4N_5$ microscopic quadratic pyramids. | 177°-178° |

[1] *Ber. Deutsch Chem. Ges.* ix. 232.
[2] *Ib.* ix. 228 and 240.

## COMPOUNDS OF TRIAD ALCOHOL RADICALS.

694 When three atoms of hydrogen in a paraffin are replaced by chlorine, bromine, hydroxyl, &c., compounds are obtained which may be looked upon as derived from triad alcohol radicals. Of such compounds many have been described in the foregoing pages. Thus, for example, chloroform or methenyl trichloride, $CHCl_3$; ethyl orthoacetate, $CH_3.C(OC_2H_5)_3$, &c. The reasons of this classification are that these bodies not only stand in close connection to the compounds under which they have been described, but that the corresponding alcohols are not known inasmuch as compounds which contain more than one hydroxyl combined with carbon do not exist, or, at any rate, are very unstable bodies. Up to within recent years only one alcohol belonging to this group was known, namely propenyl alcohol, glycerol, or glycerine. At present several others belonging to the same group have been obtained, but they have as yet been but imperfectly studied. There is, therefore, less necessity than there otherwise would be for a general description of these bodies and their derivatives. The triad radicals themselves, it may be remarked, are not known in the isolated state.

### PROPENYL ALCOHOL, GLYCEROL, OR GLYCERINE, $C_3H_5(OH)_3$.

695 Scheele, in 1779, when preparing lead plaster by heating olive oil with litharge, obtained a soluble sweet-tasting substance, and in 1784 he found that the same principle could be got from other oils, as well as from butter and lard. To this material he gave the name of "the sweet principle of fats,"[1] and it afterwards bore the name of Scheele's sweet principle or oil-sugar.

[1] *Opusc.* ii. 175.

Later on it was more carefully investigated by Chevreul, who determined its composition with tolerable exactitude, and gave to it the name which it bears of glycerine, or, as we now prefer to term it, glycerol.[1] The formula of the body was, however, first determined by Pelouze, whose experimental results corroborated Chevreul's views, that the fats are ether-like compounds of the fatty acids.[2] From this time glycerol was looked upon as a compound analogous to alcohol, but the views respecting its constitution were somewhat undecided. Berzelius supposed that it contained the radical *lipyl*, $C_3H_2$, which afterwards united with oxygen to form *lipyl oxide*, $C_3H_2O$, and he believed that two molecules of this united with three of *HO*, forming the *hypothetical anhydrous glycerol*, $C_6H_7O_5$, which with water forms its hydrate, free glycerol, $C_6H_7O_5,HO$. According to Liebig the radical *glyceryl*, $C_6H_7$, forms the starting-point of the body. This yields the *oxide*, $C_6H_7O_5$, which again combines with water to form the hydrate of glyceryl oxide.

It was not until the extended researches of Berthelot and de Luca, which will be referred to further on, that a clear light was thrown upon the constitution of glycerol. According to Berthelot it stands to ethyl alcohol in the same relation as ortho-phosphoric does to nitric acid.[3] It was Wurtz, however, who proved that glycerol is the alcohol of a triad radical[4] to which, instead of glyceryl, he gave the more suitable name of propenyl, in order to show its relation to propyl and propylene.

696 *Preparation.* Most of the fats and oils occurring in the animal and vegetable kingdoms are propenyl ethers of the fatty acids, and of those of the series $C_nH_{2n-2}O_2$, and many of these may be employed for the preparation of these acids and of glycerol. This latter compound is also a product of the alcoholic fermentation of sugar, and is contained in beer and wine. It may likewise be prepared, according to the method of Scheele, who gives the following description. "It is not generally known that all solid oils obtained by pressure contain a natural sweet principle which differs in its special relations and properties from the other well-known saccharine materials occurring in the vegetable kingdom. This sweet principle makes its appearance when oils of the kind are boiled with litharge and water until the whole of the litharge

[1] *Recherches sur les corps. gras. &c.* 209 and 338.
[2] *Ann. Chem. Pharm.* xix. 210; xx. 46.
[3] *Comptes Rendus*, xxxix. 745.
[4] *Ann. Chim. Phys.* [3], xliii. 492.

is dissolved by the oil. Water is then poured upon the *emplastrum simplex* thus formed, the whole boiled for a few minutes, and, on cooling, the liquid is filtered off from the plaster, and boiled until the residue becomes syrupy."[1] This method of preparation was used for many years with the sole alteration that sulphuretted hydrogen was passed through the solution in order to free it from lead. As, however, towards the middle of the present century, the use of glycerol for a great variety of purposes became extended, it was found necessary to obtain it in large quantities. It did not appear possible at that time to prepare it from the soap-boilers' leys, in which it is contained in very dilute solution, mixed with alkali and common salt. On the other hand, it proved easy to obtain it as a by-product in the manufacture of stearic acid, and the two manufactures were easily worked side by side.

The saponification of the fats,[2] which are glycerides of palmitic, stearic, and oleic acids, such for example as tallow, palm-oil, &c., may be carried out in many ways, as, for example, by distillation in a current of superheated steam, when the fat decomposes into the fatty acid and glycerol with assumption of the elements of water. This process, however, has only come into partial use; the one which is now most generally employed, with certain modifications, being that known as Milly's. For this purpose the fat is gradually heated to 150° with from 2 to 3 per cent. of sulphuric acid, and then distilled with water under pressure, or simply heated. The sulphuric acid is removed from the aqueous solution of glycerol thus obtained, by lime or barium carbonate, and the solution concentrated. Another process by which a purer product is obtained is that of lime saponification, the fat being heated with lime and water in closed boilers, and the lime soap thus formed decomposed by hydrochloric acid, whilst the glycerol solution is exactly neutralized with sulphuric acid in order to precipitate the lime, and then evaporated.

In order to purify commercial glycerol it is diluted to a specific gravity of 1·07, decolourized by means of animal charcoal, concentrated in a vacuum pan, and this operation repeated if necessary. The refined glycerol thus obtained is, however, by no means a pure product, and is inapplicable to certain uses.

[1] *Sämtl. Werke, Deutsch. von Hermbstädt*, 1793, ii. 355.

[2] By the term saponification was originally meant, of course, the conversion of fat into soap. At the present time the word is used to express generally the decomposition of an ethereal salt into an alcohol and an acid.

The most important improvement in the glycerol industry was made in 1855, when Wilson and Payne patented a process for purifying this substance by distillation. A current of steam at a temperature of 100° to 110° is passed through glycerol which has been concentrated at as low a temperature as possible to a specific gravity of 1·15, and this process continued until the distillate has no acid reaction. The temperature of the superheated steam is then raised from 170° to 180°, and the vapours of glycerol and water which pass over are collected in a series of condensers surrounded by non-conducting surfaces, so that the pure glycerol collects in the first condenser, whilst the second contains a mixture of glycerol and water, and the last water alone. This process was first carried out on the large scale by Price's Patent Candle Company, and the glycerol thus obtained is known in commerce as "Price's glycerine."

Another mode of purification which yields an excellent product is that introduced in 1871 by Messrs. Sarg, Son, & Co., of Vienna. In this case glycerol is cooled down from 0° to + 5°, and a small quantity of crystallized glycerol added. This produces crystallization of the mass, which, according to its purity, becomes wholly or partially solidified. The crystals which are then broken up are freed from the mother-liquor by drying in a centrifugal sieve.

Distilled glycerol often possesses a peculiar rough taste and in this case requires to be further purified by crystallization.

A new process for obtaining glycerol from soap leys has been proposed by Clolus. The leys are neutralized with hydrochloric acid in order to separate out any fatty acid. The filtrate is then evaporated until it attains a specific gravity of 1·27, and the salt which separates out is removed by means of a centrifugal sieve. The solution is treated with hot air, and the salt again allowed to crystallize out. The last traces of common salt are then removed by addition of fuming hydrochloric acid, and this got rid of by a current of hot air or by means of lead oxide. If the leys are strongly alkaline, they are first treated with carbon dioxide in order to separate out bicarbonate of soda, and the operation conducted as described. The impure glycerol is then purified by distillation or crystallization.[1] Several other processes for extracting glycerol from soap leys have been patented.[2]

[1] *Ber. Deutsch. Chem. Ges.* xv. 402.

[2] *Ib.* xv. 548, 1097. For list of patents concerning extraction of glycerol from soap leys, see *Journal of Society of Chemical Industry*, 1882-3.

It was formerly supposed that the various fats did not contain the same glycerol but that in all probability homologous glycerols were contained in them. This, however, has been shown not to be the case.[1]

*Synthesis.* Glycerol was first obtained synthetically by Friedel and Silva. For this purpose acetone is converted into isopropyl alcohol; this is then transformed into the iodide from which propylene can be prepared. On heating the dichloride with chloride of iodine propenyl trichloride is obtained, and this, on heating with twenty times its volume of water to 160°, is converted into glycerol.[2]

697 *Properties.* Glycerol is a thick liquid having a pure sweet taste. It rapidly absorbs moisture from the air, and is miscible with water and alcohol in every proportion, but is insoluble in ether and chloroform. When quickly cooled it does not crystallize, but solidifies at −40° to a gum-like mass. It was not believed to be crystallizable until crystals were accidentally observed[3] in the winter of 1867. Since that time it has been found that if it be allowed to stand in a sufficiently concentrated condition at 0°, crystals form after some days, or it may be after some weeks. These have the appearance of sugar-candy and belong to the rhombic system. They are hard and gritty between the teeth, but deliquesce on exposure to air. Their melting-point has been differently stated, probably depending on the fact that they are very hygroscopic. The highest melting point was found by Kraut to be 22°—22°·6. This, however, he believes to be too low.[4] Pure glycerol has a specific gravity at 12° of 1·269 and boils at 290°, a small quantity of polyglycerols (see p. 351) being, however, formed.[5] Under a diminished pressure of 50 mm. it boils at 210°. Nevertheless, it evaporates to an appreciable extent at 100°, and hence care must be taken in the determination of glycerol in beer, wine, &c. Lentz[6] has constructed tables giving the specific gravity of mixtures of glycerol and water.

In presence of salts it decomposes on heating, with formation of a variety of products, amongst which strongly

[1] Hofmann, *Journ. Chem. Soc.* xiii. 71.
[2] *Bull. Soc. Chim.* xx. 98.
[3] Crookes, *Chem. News.* xv. 26; Gladstone, *Journ. Chem. Soc.* [2], v. 384; Sarg, *Zeitsch. Chem.* 1867, 70.
[4] *Ber. Entw. Chem. Ind.* ii. 512.
[5] Bolas, *Journ. Chem. Soc.* [2], ix. 84.
[6] *Fresenius' Zeitsch.* xix. 302.

smelling acrolein, $C_3H_4O$, always occurs. When heated to 150° glycerol takes fire, burning with a steady blue but non-luminous flame, and glycerol when not too much diluted with water may be burnt like oil by means of a wick.[1]

If a particular species of schizomycetes be added to a tolerably dilute aqueous solution of glycerol, together with calcium carbonate and the materials necessary for the growth of the plant, fermentation takes place, butyric and caproic acids and butyl alcohol being formed, together with a very small quantity of propyl alcohol and ethyl alcohol (Fitz). In addition to these products trimethylene glycol (Freund, see p. 130) and phoron, $C_9H_{14}O$, (Part I., p. 572) are also formed. The latter is likewise produced when a mixture of quicklime, zinc-dust, and glycerol is heated in a current of hydrogen to a point not quite reaching a red-heat.[2] Another schizomycetes (*Bacillus subtilis*) yields, on the other hand, mainly ethyl alcohol and butyric acid.[3]

Many metallic oxides dissolve in glycerol; amongst these are the alkaline earths, lead oxide, cupric oxide, and ferric oxide. Many salts, especially deliquescent ones, also dissolve in it, as well as some which are not deliquescent, as saltpetre, silver nitrate, tartar emetic, mercuric iodide, gypsum, &c.

Cold nitric acid oxidizes glycerol to glyceric acid. At the same time formic acid, glycollic acid, glyoxylic acid, and racemic acid,[4] oxalic acid, tartronic acid, mesotartaric acid and hydrocyanic acid are formed.

The formation of racemic (doubtless glycotartaric) and mesotartaric acids can readily be explained. On oxidation of glycerol the first products are either glyoxal or aldehydic acid, $COH.CH(OH).CO_2H$, both of which are converted into a tartaric acid by the action of hydrocyanic acid.[5]

Glycerol is largely used for a variety of purposes; by far the largest amount employed in the manufacture of nitro-glycerol. It is also used as an article of food, being easily digestible and tasting like cane sugar, from which, however, it is distinguished inasmuch as it does not enter into fermentation under the same conditions as this latter body does, and also as its solutions do not dry up or crystallize. Hence it finds its way to the cellars

[1] Godeffroy, *Ber. Deutsch. Chem. Ges.* vii. 1566.
[2] Schulze, *Ber. Deutsch. Chem. Ges.* xv. 64.
[3] Fitz, *ib.* xi. 1892.
[4] Heintz, *Ann. Chem. Pharm.* clii. 325.
[5] Przybytek, *Ber. Deutsch. Chem. Ges.* xiv. 2071.

of the brewer and wine-dealer, as it is used to "improve" the quality of wine, and is said to impart keeping power to beer.[1] It is also employed in the manufacture of lemonade, liqueurs, fruit preserves, vinegar, mustard, &c. The fact that it prevents access of air to bodies with which it is covered makes it useful, instead of oil, for greasing the parts of moving machinery, whilst its hygroscopic properties render it available for preventing the drying up of copying ink, of snuff, and microscopic preparations, &c. For the same reason it has been also employed in working up vegetable and animal fibre, and is also used, either alone or in combination with soap, as a means of rendering the skin supple, and it has proved especially valuable in hot countries in allaying the inflammatory effects of heat upon the skin.[2] A mixture of equal weights of glue softened in water, and of glycerol of specific gravity 1·225, when heated together form an elastic mass used for casting stereotype plates.

Mixtures of glycerol and water solidify at a lower temperature than pure water. Thus, for example, a 50 per cent. solution having a specific gravity of 1·127 solidifies at − 31°.[3] For this reason such a mixture has been used for filling gas-meters; this not only preventing the freezing but also the evaporation of the liquor.

698 *Sodium Propenylate*, $C_3H_5(OH)_2ONa$, is best obtained by mixing glycerol with a solution of sodium in alcohol when it deposits in small crystals grouped in stellar groups which contain a molecule of alcohol. This latter is evolved at 100°, the sodium compound remaining behind as a white deliquescent powder. It is also obtained by acting with sodium amalgam on glycerol; sodium itself only acts slightly in the cold, but when warmed the action is so violent that the mass becomes strongly heated and the whole carbonizes.[4]

*Disodium Propenylate*, $C_3H_5(ONa)_2OH$, is obtained when the foregoing compound is heated with sodium ethylate and absolute alcohol. It forms a white very deliquescent mass.[5]

Glycerol also, like sugar, combines with lime to form a soluble compound,[6] and likewise with strontia and baryta. We are,

[1] Kraut, *loc. cit.* 509.
[2] *Ib.* 510.
[3] Fabian, *Dingler's Polyt. Journ.* clv. 345.
[4] Letts, *Chem. Soc. Journ.* xxv. 450.
[5] Loebisch and Looss, *Monatsch. Chem.* ii. 842.
[6] Carles, *Pharm. Journ. Trans.* [3], iv. 550.

moreover, acquainted with soluble glycerates which, together with potassium, contain iron, copper, or bismuth,[1] but none of these compounds have as yet been obtained pure.

*Dipropenyl Sodium Manganite*, $(C_3H_5)_2Na_2MnO_6$. This singular compound is formed when freshly precipitated manganese dioxide is heated with caustic soda and glycerol. In the moist state it is of a bright scarlet colour and forms when dry a light yellowish-red indistinctly crystalline powder. It possesses a weak alkaline and somewhat astringent taste. It is insoluble in alcohol but dissolves in a mixture of equal volumes of alcohol and glycerol, yielding a deep blood-red colour. Its aqueous yellowish-red solution decomposes easily with separation of manganese dioxide. The corresponding potassium compound is only known in solution. It has a deep ruby-red colour and is not precipitated by alcohol.

*Tripropenyl Strontium Manganite*, $(C_3H_5)_2(OH)_3SrMnO_6$. This is a light ochre-yellow crystalline substance which readily falls into powder. It is insoluble in alcohol and is almost instantly decomposed by water, and possesses a strongly alkaline reaction and a disagreeable metallic taste.

Manganese dioxide dissolves in solutions of calcium hydroxide or caustic baryta in glycerol, yielding a yellowish-red colour, but the compounds thus formed have not been obtained in the solid condition.[2]

699 *Detection of Glycerol in Beer, &c.* The action of glycerol on borax is peculiar, as it takes up free boracic acid from this substance. Hence this reaction is very well adapted to indicate the presence of glycerol in beer, wine, &c. For this purpose 50 to 100 cc. is evaporated to dryness, extracted with absolute alcohol, the alcoholic extract again evaporated and the residue dissolved in a few drops of water. The solution is made slightly alkaline with carbonate of soda and a bead of borax dipped into it. This is then brought into the flame, to which a green colour is imparted if any glycerol be present. If ammonium salts are present the ammonia must be first removed by heating the solution with sodium carbonate.[3]

[1] Puls, *Journ. Prakt. Chem.* [2], xv. 83.
[2] Schottländer, *Ann. Chem. Pharm.* clv. 230.
[3] Senier and Low, *Journ. Chem. Soc.* 1878, i. 438.

## OXIDES AND ETHERS OF PROPENYL.

700 *Glycide Alcohol*, $C_3H_6O_2$. This monad alcohol, generally known as *glycide*, is formed by decomposition of its acetate [1] as well as by the action of baryta on propenyl chlorhydrin : [2]

$$\begin{array}{l} CH_2Cl \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_2 \\ | \quad\quad > O \\ CH \\ | \\ CH_2.OH \end{array} + HCl.$$

The latter mode of formation corresponds to that of propylene oxide from its chlorhydrin.

Glycide alcohol is a liquid boiling at 161°—163°, and having a specific gravity at 0° of 1·165. It is soluble in water and combines with it to form glycerol.

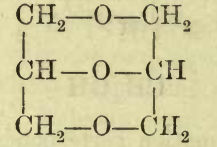
*Polyglycerols* are formed by the action of glycid alcohol or propenyl chlorhydrin on glycerol. They are viscous liquids, of which the following two have been obtained in a tolerably pure state : [3]

| | | B.P. under 10 mm. pressure. |
|---|---|---|
| Diglycerol, | $O\begin{cases} C_3H_5(OH)_2 \\ C_3H_5(OH)_2 \end{cases}$ | 220°-230° |
| Triglycerol, | $\begin{array}{l} O\begin{cases} C_3H_5(OH)_2 \\ C_3H_5(OH) \end{cases} \\ O\begin{cases} C_3H_5(OH)_2 \end{cases} \end{array}$ | 275°-285° |

*Propenyl Oxide*, $(C_3H_5)_2O_3$. This compound, which is commonly known as *glycerine ether*, was first observed by Berthelot and de Luca, but not further examined by them.[4] It is also formed when glycerol is distilled with calcium chloride,[5] and occurs as a by-product in the preparation of allyl alcohol from glycerol and

[1] Gegerfeldt, *Bull. Soc. Chim.* xxiii. 160 ; Breslauer, *Journ. Prakt Chem.* [2] xx.
[2] Hanriot, *Ann. Chim. Phys.* [5], xvii. 112.
[3] Lourenço, *Ann. Chim. Phys.* [3], lxvii. 299.
[4] *Ann. Chim. Phys.* [3], xliii. 279.
[5] Linnemann and v. Zotta, *Ann. Chem. Pharm.* Suppl. viii. 254 ; v. Zotta, *Ann. Chem. Pharm.* clxxiv. 90.

oxalic acid.[1] It is likewise obtained, together with other products, when glycerol is distilled with two per cent. of sal-ammoniac.[2] It is a liquid boiling at 171°—172°, and having a specific gravity of 1·16 at 16°. It is soluble in water, and combines with it at 100° to form glycerol. If it be saturated at 0° with hydriodic acid it decomposes, in an analogous way to the other ethers, into glycerol and propenyl tri-iodide, which latter substance, however, decomposes into iodine and allyl iodide, $C_3H_5I$.[3] Hence it possesses the following constitution:



It is remarkable that in its preparation by means of calcium chloride a small quantity of phenol, $C_6H_6O$, a body belonging to the aromatic series, is formed, together with other products.

*Ethyl Propenyl Ether*, or *Glycerol Monethylin*, $C_3H_5(OH)_2OC_2H_5$, is formed by the action of sodium ethylate on propenyl chlorhydrin, and is a body boiling at 225°—230°, soluble in water, and separating out again on the addition of carbonate of potash.[4]

*Diethyl Propenyl Ether* or *Glycerol Diethylin*, $C_3H_5(OH)(OC_2H_5)_2$, is obtained by heating glycerol with ethyl bromide and caustic potash,[5] as well as by the action of sodium ethylate on propenyl dichlorhydrin.[6] It is an oily liquid, scarcely soluble in water, having a faint ethereal peppermint-like odour. It boils at 191° and has a specific gravity of 0·92.

*Triethyl Propenyl Ether*, or *Glycerol Triethylin*, $C_3H_5(OC_2H_5)_3$. When the foregoing compound is treated with phosphorus pentachloride, *chlordiethylin*, $C_3H_5Cl(OC_2H_5)_2$, is formed. This is a body boiling at 184°, and possessing a sweet smell; when heated with sodium ethylate to 120° it is converted into triethylin. This latter is also formed when diethylin is treated with sodium and ethyl iodide. It is a pleasantly ethereal smelling liquid, boiling at 185°.[7]

[1] Gegerfeldt, *Ber. Deutsch. Chem. Ges.* iv. 919; Tollens, *ib.* v. 68.
[2] Tollens and Loe, *ib.* xiv. 1946.
[3] Silva, *Compt. Rend.* xciii. 418.
[4] Reboul, *Ann. Chim. Phys.* [3], lx. 63.
[5] Berthelot, *Ann. Chim. Phys.* [3], xli. 305.
[6] Reboul, *loc. cit.*
[7] Reboul and Lourenço, *Compt. Rend.* lii. 466.

*Ethidene Propenyl Ether*, or *Aceto-glyceral*, $C_3H_5(OH)O_2.CH.CH_3$, is obtained when aldehyde is heated with glycerol for thirty hours to 170°—180°. It is a liquid which boils at 184°—188°, is slightly soluble in water, but is easily decomposed by this liquid.[1]

## Ethereal Salts of Propenyl.

701 *α-Propenyl Chlorhydrin*, $CH_2Cl.CH(OH).CH_2OH$, was obtained by Berthelot, by heating glycerol with hydrochloric acid, and termed *chlorhydrin*.[2] In order to prepare it, glycerol is saturated with hydrochloric acid and heated for 100 hours in a water-bath. The product is then distilled in a vacuum in a water-bath, until hydrochloric acid ceases to come over, and then fractionated over the naked flame.[3] *α*-Chlorhydrin is an oily liquid having a specific gravity at 0° of 1·338. It is soluble in water, and boils, with partial decomposition, at 213°. Under a diminished pressure of 18 mm., it boils at 139°, and distils without decomposition. By the action of sodium amalgam on its aqueous solution it is converted into propylene glycol.[4]

*β-Propenyl Chlorhydrin*, $CH_2(OH).CHCl.CH_2(OH)$, is formed in smaller quantity together with the foregoing compound, from which it may be separated by fractional distillation in a vacuum, as under a pressure of 18 mm., it boils at 146°. At 0° it has a specific gravity of 1·328 (Hanriot). The same compound is also obtained by the union of allyl alcohol with hypochlorous acid. It is a syrupy liquid, having a slight smell and a sweet taste, and boiling under ordinary pressure at 230—235°.[5]

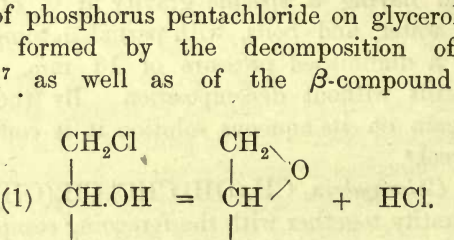
*α-Propenyl Dichlorhydrin*, $CH_2Cl.CH(OH).CH_2Cl$, was first obtained by Berthelot, by heating glycerol with an excess of fuming hydrochloric acid in the water-bath, and termed by him *dichlorhydrin*.[6] According to Reboul, a mixture of equal volumes of glacial acetic acid and glycerol is saturated with hydrochloric acid gas at 100°, and the product fractionally distilled.[7] It is also formed when chloride of sulphur is gradually added to

[1] Harnitzky and Menschutkin, *Ann. Chem. Pharm.* cxxxvi. 126.
[2] *Ann. Chim. Phys.* [3], xli. 296.
[3] Hanriot, *Ann. Chim. Phys.* [5], xvii. 62.
[4] Lourenço, *ib.* [3], lxvii. 320; Buff, *Ann. Chem. Pharm.* Suppl. v. 247.
[5] Henry, *Journ. Prakt. Chem.* [2], x. 186.
[6] *Loc. cit.* 296.
[7] *Ann. Chim. Phys.* [3], lx. 1; Watt, *Ber. Deutsch. Chem. Ges.* v. 257.

glycerol, and the whole gently heated.[1] It is an ethereal smelling liquid, boiling at 175°—176°, and having a specific gravity at 16° of 1·396. It is somewhat soluble in water, and is converted by means of sodium amalgam into secondary propyl alcohol (Lourenço, Buff). When oxidized with chromic acid solution, it yields symmetrical dichloracetone (Part I., p. 571).[2]

*β-Propenyl Dichlorhydrin*, $CH_2Cl.CHCl.CH_2OH$. According to several observers, this compound is formed together with the foregoing, when hydrochloric acid acts upon glycerol.[3] This fact is, however, denied by others.[4] It may be obtained in the pure state by the union of allyl alcohol with chlorine,[5] or by the action of hypochlorous acid on allyl chloride.[6] It is a thick, faintly ethereal smelling liquid, boiling at 182°, and having a specific gravity at 0° of 1·3799. Nitric acid oxidizes it to β-dichlorpropionic acid.

*Epichlorhydrin*, $C_3H_5ClO$, is found amongst the products of the action of phosphorus pentachloride on glycerol (Berthelot). It is also formed by the decomposition of *α*-propenyl chlorhydrin,[7] as well as of the *β*-compound by caustic potash:[8]



According to Reboul, the best method of preparing it, is to use the product boiling between 160° and 220°, obtained by the action of hydrochloric acid on a mixture of glacial acetic acid and glycerol, which, in addition to the dichlorhydrin,

[1] Carius, *Ann. Chem. Pharm.* cxxiv. 222; Claus, *ib.* clxviii. 42.
[2] Hoermann, *Ber. Deutsch. Chem. Ges.* xiii. 1707, and Markownikow, *Ann. Chem. Pharm.* ccviii. 349.
[3] Münder and Tollens, *Ber. Deutsch. Chem. Ges.* 1871, 681; Hübner and Müller, *Ann. Chem. Pharm.* clix. 168.
[4] Markownikow, *Ann. Chem. Pharm.* ccviii. 349; *Ber. Deutsch. Chem. Ges.* vi. 1210; Paschke, *Journ. Prakt. Chem.* [2], l. 82; Watt, *loc. cit.*
[5] Münder and Tollens, *loc. cit.*
[6] Gegerfeldt, *Ber. Deutsch. Chem. Ges.* vi. 720.
[7] Reboul, *loc. cit.*
[8] Münder and Tollens, *loc. cit.*

contains the acetate of propenyl. 500 cc. of this are dropped gradually into a concentrated solution of 350 grams of caustic potash, care being taken to keep the whole cool. Or the crude chlorhydrin may be added to roughly pounded caustic soda, but the temperature must not rise above 130°.[1] The yield is not more than half the theoretical one, as a large portion of the dichlorhydrin is converted into glycerol.[2]

Epichlorhydrin is an oily liquid insoluble in water, possessing an ethereal smell, somewhat resembling that of chloroform. It has a sweet burning taste, boils at 116°·6, and has a specific gravity at 0° of 1·203 (Thorpe). When shaken up with fuming hydrochloric acid, it combines with it to form *a*-propenyl dichlorhydrin, which may be obtained in this way in the pure state very readily. It unites still more easily with hydrobromic acid, and its combination with hydriodic acid takes place with yet greater avidity. If this gas be passed over epichlorhydrin cooled to 0°, normal propyl chloride and some propyl iodide are formed.[3] It unites also with water at 100° to form the monochlorhydrin, and with alcohol to form its ethyl ether, &c. In its chemical relation it therefore closely resembles ethylene oxide.

When heated with potassium acetate, it forms the above named glycide acetate, $C_3H_5O_2.\ C_2H_3O_2$, a liquid boiling at 168°—169°. Potassium cyanide converts the chloride into *epicyanhydrin*, $C_3H_5O.CN$, a body crystallizing in tablets or prisms, melting at 163°, and yielding when boiled with baryta water or hydrochloric acid, *epihydrin carboxylic acid*, $C_3H_5O.CO_2H$; a body crystallizing in glistening needles, melting at 225°.[4] This body is isomeric with aceto-acetic acid, and is reduced to butyric acid by means of hydriodic acid:

$$\underset{\diagdown\ \diagup \atop O}{CH_2.CH}.CH_2.CO_2H + 4HI = CH_3.CH_2.CH_2.CO_2H + 2I_2 + H_2O.$$

702 *Propenyl Trichloride*, or *Trichlorhydrin*, $C_3H_5Cl_3$, is obtained by the action of phosphorus pentachloride on propenyl dichlorhydrin,[5] or epichlorhydrin.[6] It is also formed by the

[1] Prevost, *Journ. Prakt. Chem.* [2], xii. 160.
[2] Claus, *Ber. Deutsch. Chem. Ges.* x. 556.
[3] Silva, *Compt. Rend.* xciii. 418.
[4] Paschke, *Journ. Prakt. Chem.* [2], i. 97; Hartenstein, *ib.* vii. 295.
[5] Berthelot and de Luca, *Ann. Chim. Phys.* [3], lii. 437.
[6] Reboul, *ib.* lx. 37.

action of chlorine on propylene chloride,[1] secondary propyl chloride,[2] and propane,[3] when other substitution-products are also of course formed.

In order to prepare it, a mixture of glycerol and glacial acetic acid is saturated with hydrochloric acid, and the whole slowly distilled until the boiling point reaches 130°; the residue is then washed with water and carbonate of soda solution, dried over calcium chloride, and the liquid then allowed slowly to flow into phosphorus chloride.[4]

Propenyl trichloride is a liquid boiling at 158°, and having a smell resembling that of chloral. At 0° it has a specific gravity of 1·41. When heated with twenty times its volume of water it is converted into glycerol.

*α-Dichlorglycide*, or *α-Epidichlorhydrin*, $C_3H_4Cl_2$, was obtained by Berthelot and de Luca, as a by-product in the preparation of trichlorhydrin.[5] Reboul then obtained it by the action of caustic potash on the latter body, and described it as an ethereal alliaceous smelling body boiling at 101°—102°.[6] More recent observations have shown that two isomeric bodies are produced in this reaction :[7]

α-Epidichlorhydrin. $CH_2{=}CCl.CH_2Cl$. β-Epidichlorhydrin. $CHCl{=}CH.CH_2Cl$.

Of these the *α*-compound is obtained in the larger quantity. It boils at 94°, and has a specific gravity at 0° of 1·236. It combines with fuming hydrochloric acid at 100° to form *chlordimethylmethylene chloride*, $CH_3.CCl_2.CH_2Cl$, a body also obtained by the action of chlorine on dimethylmethylene chloride (p. 131), and boiling at 123°.[8]

It also unites with chlorine to form *α-tetrachlorglycide*, $C_3H_4Cl_4$, a body boiling at 164°, and having an ethereal smell and a sweet burning taste.

*β-Dichlorglycide*, or *β-Epidichlorhydrin*, is formed in larger quantity by the action of phosphorus oxychloride or phosphorus pentachloride on dichlorhydrin :[10]

$$CH_2Cl.CH(OH).CH_2Cl = CHCl{=}CH.CH_2Cl + H_2O.$$

[1] Cahours, *Compt. Rend.* xxxi. 292 ; Bielohoubek, *Ber. Deutsch. Chem. Ges.* ix. 924.
[2] Linnemann, *Ann. Chem. Pharm.* cxxxvi. 48 ; cxxxix. 19 ; Friedel and Silva, *Compt. Rend.* lxxiv. 865.
[3] Schorlemmer, *Proc. Roy. Soc.* xvii. 372.
[4] Fittig and Pfeffer, *Ann. Chem. Pharm.* cxxxv. 359.
[5] *Ann. Chim. Phys.* [3], lii. 438.
[6] *Ib.* lx. 37.
[7] Friedel and Silva, *Bull. Soc. Chim.* [2], xvii. 386.
[8] Friedel and Silva, *ib.*
[9] Fittig and Pfeffer, *Ann. Chem. Pharm.* cxxxv 357.
[10] Hartenstein, *Journ. Prakt. Chem.* [2], vii. 310.

It is a mobile liquid having a sweet, somewhat burning taste, and pleasant smell; it boils at 109°, and at 0° its specific gravity is 1·250. It does not form any compound with hydrochloric acid, but combines with chlorine to form *β-tetrachlorglycide*, $C_3H_4Cl_4$, a body boiling at 171°.

*Propenyl Monobromhydrin*, $C_3H_5Br(OH)_2$, is obtained, together with other products, by the action of phosphorus pentabromide on glycerol. It is a thick oily aromatic tasting liquid, which boils under a pressure of 10 mm. at 180° (Berthelot and de Luca).

*α-Propenyl Dibromhydrin*, $CH_2Br.CH(OH).CH_2Br$, is formed together with the foregoing compound, and is an ethereal smelling liquid boiling at 219°.

*β-Propenyl Dibromhydrin*, or *Dibrompropyl Alcohol*, $CH_2Br.CHBr.CH_2(OH)$, is formed by the combination of allyl alcohol with bromine, and is a liquid boiling at 212°—214°.[1]

703 *Propenyl Tribromide*, or *Tribromhydrin*, $C_3H_5Br_3$, is formed together with the mono- and dibromhydrins by the action of phosphorus bromide on glycerine (Berthelot and de Luca). It is best prepared by treating allyl iodide with bromine.[2] It is a faintly ethereal smelling, thick liquid, which has a specific gravity at 10° of 2·407, and boils at 219°—220°, and on cooling crystallizes in long glistening prisms melting at 16°—17°.[3] When heated with solid caustic potash *β-epidibromhydrin*, $CHBr{=}CH.CH_2Br$., is produced. This is an oily alliaceous smelling liquid, which boils at 151°—152°, and combines with bromine to form *tetrabromglycide*, $C_3H_4Br_4$, a compound boiling at 250°—252°, with decomposition.[4]

*α-Propenyl Di-iodhydrin*, $CH_2I.CH.(OH).CH_2I$, is formed by heating dichlorhydrin with a concentrated solution of potassium iodide. It is a thick oily liquid which crystallizes in a freezing mixture, and decomposes when heated.[5]

*β-Propenyl Di-iodhydrin*, $CH_2I.CHI.CH_2.(OH)$, is formed by acting with allyl alcohol on iodine, which are brought together in solution in chloroform. The compound crystallizes in needles which when exposed to light acquire a brown colour.[6]

[1] Kekulé, *Ann. Chem. Pharm.* Suppl. i. 138; Markownikow, *Zeitsch. Chem.* 1864, 68; Tollens and Münder, *Ann. Chem. Pharm.* clxvii. 224; Michael and Norton, *Amer. Chem. Journ.* ii. 18.

[2] Wurtz, *Ann. Chim. Phys.* [3], li. 91.

[3] Henry, *Ber. Deutsch. Chem. Ges.* iii. 298.

[4] Reboul, *Ann. Chim. Phys.* [3], lx. 42.

[5] Claus, *Ann. Chem. Pharm.* clxviii. 24.

[6] Hübner and Lellman, *Ber. Deutsch. Chem. Ges.* xiii. 460.

*Propenyl Mono-iodhydrin* is obtained, according to Reboul, by heating the chlorhydrin with potassium iodide. It is an oil which has not been further investigated.

Propenyl tri-iodide is not known.

By the action of hydriodic acid or iodide of phosphorus on an excess of glycerol, allyl iodide, $C_3H_5I$, is formed, together with propylene. If, on the other hand, the two first compounds are present in excess, propylene and isopropyl iodide are formed. In this it is possible that the following reaction takes place. At first propenyl tri-iodide is formed, and this decomposed into iodine and allyl iodide. This latter is then reduced by the hydriodic acid to propylene, and this combines with hydriodic acid to form isopropyl iodide.[1] According to Henry, some allyl alcohol is also formed, and from this it must be assumed that di-iodhydrin is first formed, and that this splits up into iodine and allyl alcohol, which latter is then changed into the iodide.[2]

*Sulphates of Propenyl.* Only the acid ethereal salts are known. Pelouze obtained one of these, which he termed *glycerine sulphuric acid*, $C_3H_5(OH)_2SO_4H$, by dissolving one part of glycerol in two parts of sulphuric acid. He then neutralized with lime, and obtained the easily soluble calcium salt, crystallizing in needles, and by decomposing this with oxalic acid he obtained the free acid in solution, which possesses an acid taste, but is very unstable, decomposing by moderate concentration in a vacuum even below 0° into glycerol and sulphuric acid. Its salts are also very unstable.[3]

*Acid Propenyl Trisulphate*, $C_3H_5(SO_4H)_3$, is formed by the action of chlorsulphonic acid on glycerol, and is a snow-white, very hygroscopic, crystalline mass. Its acid solution is easily converted into *acid propenyl disulphate*, $C_3H_5(OH)(SO_4H)_2$. Both acids form amorphous salts.[4]

*Propenyl Mononitrate*, $C_3H_5(OH)_2NO_3$, is obtained by the action of dilute nitric acid on glycerol. It is a liquid easily soluble in water, and very difficultly soluble in ether, which does not explode on percussion.[5]

704 *Propenyl Trinitrate* or *Trinitrin*, $C_3H_5(NO_3)_3$. This compound, which is commonly known under the name of *nitro-glycerine*, was discovered by Sobrero, who obtained it by dissolving glycerol

[1] Erlenmeyer, *Ann. Chem Pharm.* cxxxix. 211.
[2] *Ber. Deutsch. Chem. Ges.* xiv. 403.
[3] *Ann. Chim. Phys.* lxiii. 21.
[4] Claesson, *Journ. Prakt. Chem.* [2], xx. 4.
[5] Hanriot, *Ann. Chim. Phys.* [5], xvii. 118.

in a mixture of nitric and sulphuric acids. Amongst its properties he noticed that a small quantity, when brought under the tongue, produces a violent headache.[1] The vapour produces the same effect, though it has been noticed that this ceases after a time in the case of workmen who are exposed to its influence. Nitro-glycerine was for some time employed in America, and known as glonoin-oil. The composition of this substance was first ascertained by Williamson, who noticed that on boiling with caustic potash it is converted into nitric acid and glycerine.[2] Its properties were more fully examined by de Vrij[3] and E. Kopp,[4] and its use as an explosive was suggested in 1867 by Nobel.[5]

*Preparation.*—Many receipts are given for preparing this substance. According to Nobel it is best made by allowing one part of glycerine to flow in a thin stream into a well-cooled mixture of four parts of sulphuric acid and one part of pure concentrated nitric acid, the mixture being contained in a wooden vessel lined with lead, from which the product is allowed to flow into a large tank placed at a lower elevation, holding several tons of water.[6] Or the mixture of acid and glycerine may be allowed to stand quietly, when the nitro-glycerine collects at the bottom as a heavy layer.[7]

In large dynamite works as much as 1,500 pounds of nitro-glycerine is made in one operation. Should the chemist be unable to control the action, which, unless care be taken, is apt to become violent, he runs the charge into water, and thus stops the reaction by dilution. During the process of mixing the acid and glycerine, the charge has to be constantly mixed by stirring, and this is so effected by machine power as to be under the control of the operator, so that neither speed nor quantity can be exceeded. The nitro-glycerine next requires to be well washed with water to free it from acid, and this is effected by blowing air through the mixture contained in the washing-tanks. Great care and special precautions are necessary in this manufacture, for until the nitro-glycerine has been absorbed by the Kieselguhr used for the preparation of dynamite (see p. 361), it is a most dangerous substance, exploding with frightful force

[1] *Compt. Rend.* xxiv. 247.
[2] *Proc. Roy. Soc.* vii. 130.
[3] *Chem. Centralb.* 1855, 570.
[4] *Compt. Rend.* lxiii. 189.
[5] Dingler's *Polyt. Journ.* clxxxiii. 221.
[6] *Ib.* ccxxi. 274.
[7] *Ber. Deutsch. Chem. Ges.* ix. 1800; Wagner, *Jahresb.* 1879, 406; 1880, 375; see also *Government Report on Explosives*, 1874.

on even slight percussion. In the form of dynamite it is however much less liable to accidental explosion.

Nitroglycerine is a light-yellow, heavy, oily liquid, having a specific gravity of 1·6 at 15°. It has a sweet, burning taste, and is insoluble in water, but dissolves in alcohol, and still more readily in ether. It crystallizes at −20° in long needles (Champion). It is poisonous, but the lethal dose is a considerable one. About ten drops produce poisonous symptoms in the human subject, though they do not act fatally.[1]

It is not easily inflammable, and, when ignited, burns without explosion. When poured on to a tolerably hot surface it evaporates, but when dropped on to one more strongly heated, a violent explosion takes place. A temperature of 257° produces the most violent effect, the explosion becoming less at higher temperatures, and when dropped on to a red-hot plate the mass becomes spheroidal, and burns without explosion.[2]

The explosive effect of nitro-glycerine on percussion is however far more violent than that produced when it is simply heated (Abel).[3] The statement that it is more readily explosive under percussion in the solid than in the liquid state appears from Beckerhinn's experiments not to be correct,[4] and the frightful accidents which have occurred from the explosions of the solid mass appear to have been simply brought about by carelessness. The change which takes place during the explosion is represented by the following equation:[5]

$$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O.$$

Nitro-glycerine, when pure, can be preserved without decomposition, but if it is not washed completely from acids it gradually decomposes with formation of oxalic acid, glyceric acid, and other products.[6] Caustic alkalis cause the re-formation of glycerine. This is also formed, together with nitric oxide, by the action of concentrated hydriodic acid upon nitro-glycerine.[7]

705 Nitro-glycerine was first known in the pure state under the name of *Nobel's explosive oil*, used largely for mining and other operations. Owing to the many accidental explosions which

[1] Schuchhard, *Jahresb.* 1866, 525.
[2] Kopp, *Dingl. Polyt. Journ.* clxxxii. 237; Champion, *Bull. Soc. Chim.* [2], xvi. 369; see also Gorup-Besanez, *Ann. Chem. Pharm.* clvii. 289.
[3] *Phil. Trans.* 1869; *Chem. Soc. Journ.* xxiii. 41.
[4] *Jahresb.* 1876, 1106.
[5] Berthelot, *Force de la Poudre*, &c. 160.
[6] Müller and Warren de la Rue, *Ann. Chem. Pharm.* cix. 122.
[7] Mills, *Journ. Prakt. Chem.* xciv. 468.

occurred in its use and during its transit, the carriage of this material was forbidden in many places, and therefore Kopp suggested that it should be manufactured on the spot where it was to be used, and Nobel introduced a product termed *methylated explosive oil*, consisting of a solution of nitro-glycerine in wood-spirit, which will not explode on percussion. On addition of water or by evaporating off the wood-spirit, the nitro-glycerine can again be obtained. This being a liquid is inapplicable for many purposes, and Nobel succeeded in preparing a much more useful material, which can be forwarded from place to place without danger, though still possessing the explosive power of the original nitro-glycerine. This substance is known in commerce as dynamite. Dynamite consists of a mixture of three parts of nitro-glycerine and one part of Kieselguhr (Vol. I., p. 566), this latter being a finely-divided, infusorial, silicious earth, which has a high absorptive power, and is capable of taking up the nitro-glycerine without becoming pasty.[1] The Kieselguhr is first heated in order to destroy organic matter, and on cooling the nitro-glycerine is added, the mixture being made in leaden vessels with wooden beaters. Cartridges made of parchment paper are filled with this material, and the cartridge is fitted in the ordinary way with a detonating fuse. Dynamite is far safer than the pure nitro-glycerine, as from its softness it yields to an accidental blow, and is therefore not so liable to explode as nitro-glycerine itself.

From recent experiments it appears that the energy developed by the explosion of one ton of nitro-glycerine is equal to 64,452 foot-tons, that of dynamite being equal to 45,675 foot-tons. According to the above reaction the theoretical initial pressure exerted by nitro-glycerine on exploding is from six to seven times that of gunpowder.

In order to exhibit the non-explosive character of dynamite under ordinary percussion, the following experiments have been made. A barrel containing 540 kilos. of dynamite was allowed to fall from a height of twenty feet on to a paved road without explosion occurring. A weight of ten kilos. was allowed to fall from twenty feet on to a dynamite cartridge, when it was simply flattened. In another experiment seven and a half kilos. of dynamite contained in a cask was ignited by means of a burning cigar. The dynamite burnt with a bright flame, but the barrel was not blown to pieces or even burnt. In the same way a tin

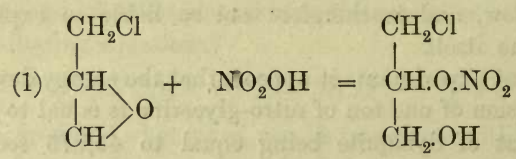
[1] *Dingl. Polyt. Journ.* cxc. 124.

box containing dynamite was thrown into a common fire without any evil effect being produced, the dynamite simply burning.[1] If, however, dynamite be exploded by means of a percussion fuse containing fulminating mercury, it produces powerful explosive effects, even when placed on an open surface; balks of timber, iron cylinders, and masses of granite, can in this way be broken.

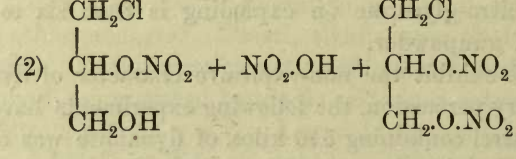
A number of other nitro-glycerine preparations have been suggested. These are known under the names of Lithofracteur, Dualin, Blasting Gelatine, &c. They produce the same effects as nitro-glycerine, and are obtained by the addition of this body to nitrated sawdust, gunpowder, nitrates, guncotton, and other materials.

According to the statements of Nobel the production of dynamite increased from eleven tons in 1867 to 3,120 tons in 1874.[2] At the present moment it is even larger, as appears from the fact that in 1880 the total European production of glycerine amounted to about 9,000 tons.[3]

706 *Monochlordinitrin*, $C_3H_5Cl(NO_3)_2$. This is obtained by the action of monochlorhydrin on a mixture of concentrated nitric and sulphuric acids, or by allowing concentrated nitric acid to drop into epichlorhydrin well cooled with ice:



(1) $CH_2Cl.CH(O).CH + NO_2OH = CH_2Cl.CH(O.NO_2).CH_2.OH$



(2) $CH_2Cl.CH(O.NO_2).CH_2OH + NO_2.OH + CH_2Cl.CH(O.NO_2).CH_2.O.NO_2 + H_2O$

It is an oily, easily-inflammable, but not explosive material.

*a-Dichlormononitrin*, $CH_2Cl.CH(NO_3)CH_2Cl$, is obtained by the action of a mixture of sulphuric and nitric acids on the corresponding dichlorhydrin. It is a compound similar to the

[1] *Ber. Deutsch. Chem. Ges.* ix. 1802.
[2] *Monit. Scientif.* [3], vi. 248; see also Engels, *Wagner's Jahresb.* 1880, 378.
[3] *Wagner's Jahresbericht*, 1880, 447.

foregoing, and boils with decomposition at a temperature of 180°—190°.[1]

*β.-Dichlornitrin*, $CH_2Cl.CHCl.CH_2(NO_3)$, is an oily liquid which has a peculiar aromatic smell, sweet taste, and boils at 180°.[2]

*The Phosphates of Propenyl.* Of these only the dibasic *glycerol phosphoric acid*, $C_3H_5(OH)_2PO_4H_2$, is known. This was obtained by Pelouze by the action of phosphorus pentoxide or metaphosphoric acid on glycerol.[3] Gobley then observed that this acid occurs in a peculiar compound contained in the yolk of egg and in the brain,[4] and since that time it has been found that this latter compound is not only contained in the animal but is also widely distributed in the vegetable kingdom (see *Lecithin*, p. 370). Glycerol phosphoric acid is also found in small quantity in normal human urine,[5] and, together with a large quantity of lactic acid, in muscular fibre.[6] The free acid which is obtained by decomposing the easily-soluble barium salt with sulphuric acid is only known in dilute solution, as it decomposes on concentration.

The calcium salt, $C_3H_5(OH)_2PO_4Ca$, is a very characteristic one. It is easily soluble in cold water, and separates, on warming the solution, in snow-white, pearly, glistening tablets or scales, which dissolve again on cooling.

*Propenyl Arsenite*, $C_3H_5AsO_3$. Glycerol dissolves large quantities of arsenic trioxide. Such a solution has been used by calico-printers for fixing aniline colours, and this contains the above-mentioned compound, which may be obtained in the pure state by heating nineteen parts of glycerol with twenty parts of arsenic trioxide until no further quantity of water is evolved, and then, on cooling, withdrawing the excess of glycerol by means of acetone. In this way an amber-yellow, fat-like mass is left, which melts at 50°, forming a thick liquid. It dissolves in glycerol as well as in water, but is decomposed by this latter liquid.[7]

[1] Henry, *Ber. Deutsch. Chem. Ges.* iii. 347. [2] *Ib.* iv. 701.
[3] *Compt. Rend.* xxi. 718. [4] *Neu. Jahrb. Pharm.* ix. 161 ; xi. 405 ; xii. 5.
[5] Sotnitschewsky, *Hoppe-Seyler's Zeitsch.* iv. 214.
[6] Diakonow, *Chem. Centralblatt*, 1867, 816.
[7] Schiff, *Bull. Soc. Chim.* [2], viii. 99.

## THE FATS OR GLYCERIDES (PROPENYL ETHEREAL SALTS OF THE FATTY ACIDS).

707 The existence of animal fats naturally attracted the attention of even uncivilized man, and the ancients were, of course, well acquainted with their peculiar properties. Still we know nothing about the origin of this knowledge or when the fats were first used in the arts. More remarkable is the acquaintance made by man in very early times with the vegetable fats and oils, as is shown by the mention of the fact in the oldest books of the Old Testament. The Greeks and Romans in the early centuries after Christ were well acquainted with olive oil, as well as with almond oil, walnut oil, castor oil, &c. These were obtained by pressing or by boiling the fruit or seeds with water. Herodotus and Hippocrates described, in the fifth century B.C., the butter (*βούτυρον*) which the Scythians obtained from mare's milk by violent agitation, and Dioscorides also relates that the best butter is obtained from the fattiest milk, as sheep's milk, but that it can also be got from goat's milk.

So, too, the saponification of animal fats was known in early times (see Part I., p. 688). It was, however, long believed that in this process the whole of the fat combined with the alkali, and the conclusion drawn from this, as well as from the fact that metals are attacked by fat, was that these latter substances contain an acid.

In the first half of the last century it was, however, noticed that the fat separated out from a soap by means of an acid possessed different properties from that which was employed in making the soap, but the proper explanation of this was not given until after Scheele's discovery of the sweet principle of oil. This was however accomplished by the celebrated investigations of Chevreul, "sur les corps gras," begun in the year 1811, in which he proved that the fats are in fact ethereal salts.

It has already been stated that most of the natural fats are normal propenyl ethers of the fatty acids, or of the acids of the series, $C_2H_{2n-2}O_2$. For these bodies Gerhardt introduced the name *glycerides*. Lastly, Berthelot showed that not only these ethers, but also those which contain only one or two acid radicals, can be artificially prepared.[1]

[1] *Ann. Chim. Phys.* [3], xli. 216.

*Monoformin*, $C_3H_5(OH)_2CHO_2$, is obtained by heating glycerol and oxalic acid to 190°, the product being exhausted with ether. It is an oily liquid which is soluble in water, and on heating with this liquid decomposes into formic acid and glycerol. When heated under ordinary pressure it decomposes into allyl alcohol, carbon dioxide, and water, but under a diminished pressure of 10 mm. it may be distilled without decomposition at a temperature of 165°.[1]

*Diformin*, $C_3H_5(OH)(CHO_2)_2$. When the residue obtained in the preparation of formic acid, according to Lorin's method (Part I., p. 270), is heated to 140° and then shaken up with ether, deformin is obtained in solution. This substance is a colourless liquid boiling under a diminished pressure of 20—30 mm. at 163°—166°. Heated under the ordinary pressure decomposition begins about 160°; allyl formate is formed, together with allyl alcohol, formic acid, carbon dioxide, and a small quantity of carbon monoxide. It is easily decomposed by water with formation of formic acid and glycerol, and when heated with anhydrous oxalic acid it readily yields formic acid and carbon dioxide. Its formation is probably one of the preliminary processes in the preparation of formic acid from oxalic acid.[2]

*Monacetin*, $C_3H_5(OH)_2C_2H_3O_2$, is formed in small quantity when glycerol is allowed to stand for some months in contact with glacial acetic acid, and in large quantity when the mixture is heated to 100° for 114 hours. The product is treated with carbonate of potash and a small quantity of caustic potash and then extracted with ether. On evaporation of the ethereal solution the compound remains behind as a weak, ethereal-smelling liquid, having a specific gravity of 1·20.

*Diacetin*, $C_3H_5(OH)(C_2H_3O_2)_2$, is formed by heating glacial acetic acid and glycerol to 200°—275°, and is purified in the same way as monacetin. It is a liquid possessing a biting taste. It boils at 280° and at 13° has a specific gravity of 1·188. Like the foregoing compound it dissolves in a small quantity of water, and on addition of a larger quantity it becomes turbid.

*Triacetin*, $C_3H_5(C_2H_3O_2)_3$, appears to exist in small quantity in certain fats[3] in cod-liver oil,[4] and the oil of the spindle-tree (*Euonymus europœus*).[5] These oils yield on saponification a small

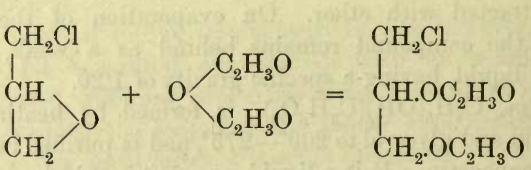
[1] Tollens and Henninger, *Zeitsch. Chem.* 1869, 88.
[2] Van Romburgh, *Compt. Rend.* xciii. 847.
[3] Chevreul, *loc. cit.*
[4] de Jongh, *Ann. Chém. Pharm.* xlviii. 362.
[5] Schweizer, *ib.* lxxx. 288.

quantity of acetic acid. Berthelot obtained it by acting for some hours on diacetin with 15—20 parts of glacial acetic acid at 250°, and Würtz prepared it by acting with silver acetate on propenyl tribromide.[1] It may, however, be most simply obtained by mixing one part of glycerol with two parts of glacial acetic acid, allowing this to boil gently for forty hours and then distilling. The liquid coming over between 257°—260° is dissolved in water and the triacetin extracted with ether.[2] It is a liquid tolerably soluble in water, possessing a weak, bitter, pungent taste, and having at 8° a specific of 1·174, and it boils at 267°—268°.

*Acetochlorhydrin* or *Chlormonacetin*, $C_3H_5Cl(OH)C_2H_3O_2$, is obtained, together with dichlormonacetin, by the action of acetyl chloride on glycerol,[3] or by heating epichlorhydrin with glacial acetic acid to 100°.[4] It is a liquid smelling like acetic ether and boiling at 250°.

*Acetodichlorhydrin*, or *β-Dichloractin*, $CH_2Cl.CHCl.CH_2(C_2H_3O_2)$, is best obtained by the union of acetyl chloride with epichlorhydrin, and is a pleasantly-smelling liquid boiling at 202°—203°.[5] The isomeric *α-dichloracetin*, $CH_2Cl.CH(C_2H_3O_2).CH_2Cl$, is formed by the action of acetyl chloride on *α*-dichlorhydrin, and boils at 194°—195°.[6]

*Diacetochlorhydrin*, or *Monochlordiacetin*, $CH_2Cl.CH(C_2H_3O_2).CH_2(C_2H_3O_2)$, is formed by the action of acetyl chloride on equal volumes of glacial acetic acid and glycerol (Berthelot and de Luca), or by heating epichlorhydrin with glacial acetic acid to 180°:



It is a faintly-smelling liquid boiling at 245°.

The *butyrins* and *valerins* are oily liquids. *Tributyrin*, $C_3H_5(C_4H_7O_2)_3$, occurs in butter, and is a neutral liquid possessing a sharp, bitter taste. *Trivalerin*, $C_3H_5(C_5H_9O_2)_3$, is contained in dolphin oil, and has a weak but unpleasant smell.

[1] *Ann. Chim. Phys.* [3], li. 97.
[2] Schmidt, *Liebig's Ann.* cc. 97.
[3] Berthelot and de Luca, *Ann. Chim. Phys.* [3], lii. 433.
[4] Reboul, *Ann. Chim. Phys.* [3], lx. 49.
[5] Truchot, *Compt. Rend.* lxi. 1170.
[6] Henry, *Ber. Deutsch. Chem. Ges.* iv. 704.

The sources of the following normal propenyl ethereal salts will be found under the corresponding fatty acids as well as under the fats.

| | | | M.P. |
|---|---|---|---|
| *Trilaurin,* | $C_3H_5(C_{12}H_{23}O_2)_3$ | Needles. | 45° |
| *Trimyristin,* | $C_3H_5(C_{14}H_{27}O_2)_3$ | Plates. | 55° |

708 *Monopalmitin,* $C_3H_5(C_{16}H_{31}O_2)(OH)_2$, occurs when palmitic acid is treated with an excess of glycerol and the mixture heated for twenty-four hours to 200°. After removal of the gycerol the product, which still contains palmitic acid, is fused and mixed with ether and a small quantity of slaked lime and heated for an hour to 100°, and the monopalmitin is then extracted by ether. This method of purification is used in the preparation of other artificial glycerides of the higher fatty acids (Berthelot). Monopalmitin crystallizes in needles which melt at 58°.

*Dipalmitin,* $C_3H_5(C_{16}H_{31}O_2)_2OH$, was obtained by Berthelot by heating glycerol with an excess of palmitic acid for 114 hours to 100°. It forms microscopic scales which melt at 59°.

*Tripalmitin,* $C_3H_5(C_{16}H_{31}O_2)_3$, is obtained from palm oil, or, better, from Chinese vegetable wax (from *Stillingia sebifera*) by first pressing out and then repeatedly treating it with hot alcohol and recrystallizing the residue from ether.[1] It is also formed when monopalmitin is treated with an excess of palmitic acid, and the mixture heated to 250°—270° for eight hours. It forms pearly, glistening crystals, melting at 50°·5, which, on further heating, again crystallize and then melt at 66°·5 (Maskelyne).

*Monostearin,* $C_3H_5(C_{18}H_{35}O_2)(OH)_2$, is prepared by heating equal parts of glycerol and stearic acid for about thirty-six hours to 200° in a sealed tube. It forms white needles melting at 61° and solidifying at 60° (Berthelot).

*Distearin,* $C_3H_5(C_{18}H_{35}O_2)_2OH$. If one part of monostearin be heated with three parts of stearic acid for three hours to 260°, white microscopic laminæ of this compound separate out. These melt at 58° and solidify at 55°.

709 *Tristearin,* $C_3H_5(C_{18}H_{35}O_2)_3$, occurs in a greater or less degree of purity in many natural fats, from which it may be obtained by repeated crystallization from ether. The stearin obtained by Chevreul by repeated crystallization of mutton suet consisted of a mixture of tristearin and tripalmitin. Lecanu found that the melting-point was raised to 62° when it was

[1] *Journ. Prakt. Chem.* lxv. 291.

recrystallized from a small quantity of ether. Duffy then observed that the melting-point rose to 69°·7 when large quantities of ether are employed and the whole recrystallized thirty-two times.[1] But this product also contains, according to Heintz, a certain quantity of tripalmitin, and in order to obtain tristearin, stearic acid must be heated with glycerol in an atmosphere of carbon dioxide for twenty-four hours to 200°, and the product then purified by Berthelot's process, and then heated with a large excess of stearic acid to 270°.[2] According to Bouis and Pimentel pure tristearin is obtained by recrystallization of the fat from the seeds of *Brindonia indica*.[3]

Tristearin is artificially prepared by heating monostearin with from fifteen to twenty times its weight of stearic acid in a tube to 270° for three hours.[4]

Tristearin crystallizes from boiling ether in tasteless, inodorous, pearly tablets. Like tripalmitin, it possesses both a variable and permanent melting-point, its volume undergoing, under these circumstances, remarkable changes, which have been investigated by Kopp. The stearin he employed was, however, not perfectly pure, and for this reason he found the melting-point too low, and this error has been corrected in the following remarks.

When stearin is heated from 0° to 55° it expands from 1·0000 to 1·0308 volume. It fuses at 55° and contracts to a volume of 1·0076. On further heating it again expands and solidifies at 71°·6, which is its true melting-point, when it possesses in the solid state a volume of 1·0759, its volume in the liquid state at the same temperature being 1·1293. It solidifies again at 70° to an indistinctly crystalline mass. When heated 4°—5° above its melting-point it solidifies again at 55° and then forms a wax-like mass.

## FATS AND OILS.

710 Of these we shall here only mention the more important, and especially those which, in addition to trioleïn, contain glycerides of the fatty acids. The composition of these fats and oils varies considerably. Some consist entirely of tripalmitin and trioleïn; as, for instance, olive oil and Chinese vegetable wax, the latter being obtained from the fruit of *Stillingia sebifera*, a tree which

[1] *Quart. Journ. Chem. Soc.* v. 197 [2] *Ann. Chem. Pharm.* xcii. 300.
[3] *Compt. Rend.* xliv. 1355. [4] Berthelot, *Ann. Chim. Phys.* [3], xli. 216.

is now cultivated both in India and America, and from the fat of which both candles and soap are prepared. Palm oil also contains these two glycerides, and probably also tristearin together with the free acids. It is obtained from the west coast of Africa, and is derived from the fruit of certain kinds of palm, as *Elæis guineensis*, forming an important article of commerce, being imported in very large quantities into this country and used for the manufacture of soap, candles, &c. The nuts or kernels of the fruit yield palm-nut oil which, in addition to the three above-named glycerides, also contains caproic, caprylic, capric, lauric, and myristic acids.[1]

Mutton suet consists chiefly of tristearin with a small quantity of oleïn and palmitin, whilst human fat contains the latter with some oleïn and stearin. Beef suet contains the same glycerides and the same quantity of oleïn as mutton suet, whilst the percentage of palmitin and stearin stands in about a mean between the latter fat and human fat (Heintz). Lard consists of these three glycerides, which are also contained in bassia fat, obtained in India from the seeds of various species of *Bassia*, used in India as food, and in Europe for candle- and soap-making.

Shea butter, or, as it was named by Mungo Park, galam butter, is said to consist entirely of stearin and oleïn;[2] this has a very pleasant taste, and may be kept for a considerable length of time without becoming rancid. It is prepared from the seeds of *Bassia parkii*, which has become an article of commerce of considerable importance in Sierra Leone.

Coco-nut oil, obtained from the fruit of *Cocos nucifera*, which grows in all tropical countries, consists to the largest extent of laurin, together with the glycerides of myristic, palmitic, capric, caprylic, and caproic acids.[3] The latter five are also contained in butter, together with tributyrin, tristearin, and a small quantity of triarachin (Heintz).[4] Goose-fat contains the glycerides of the same volatile acids together with palmitin, stearin, and oleïn.[5]

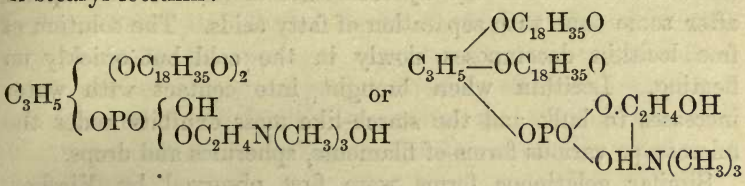
[1] Oudemans, *Jahresb.* 1870, 862.
[2] *Ib.* 1863, 333.
[3] Fehling, *Ann. Chem. Pharm.* liii. 399; Görgey, *ib.* lxvi. 290; Oudemans, *Jahresb.* 1860, 322; 1863, 311; Bizio, *ib.* 1864, 340.
[4] Lerch, *Ann. Chem. Pharm.* xlix. 212; Hehner, *Frcs. Zeitsch.* xvi. 145; Fleischmann and Vieth, *ib.* xvii. 287; Reichert, *ib.* xviii. 70.
[5] Gottlieb, *Ann. Chem. Pharm.* lvii. 43.

## THE LECITHINS.

711 Vauquelin was the first to observe that the substance of the brain contains a phosphoretted fat.[1] Fremy then showed that this yields, on decomposition with alkalis, oleic acid, glycerol, and phosphoric acid, and to it he gave the name of *oleo-phosphoric acid.*[2] He and Valenciennes also found a similar phosphoretted fat in the flesh of fish,[3] and Gobley gave to this body the name of *lecithin* (from λέκιθος, yolk of egg), inasmuch as this same compound occurs in this material, and it is also contained in ox-bile, venous blood, and other substances. He was not able to obtain it in the free state, but he showed that it yields glycerol-phosphoric acid, margaric acid, and oleic acid as products of decomposition. Hoppe-Seyler was the first to obtain lecithin in the crystalline condition from the yolk of egg and from caviare,[4] and he showed that this substance occurs widely distributed in nature, not only in the animal- but also in the vegetable-world, occurring in cells in process of growth. He found it, amongst other sources, in yeast and various fungi, in many seeds, in all the organs and liquids of the human body, with the exception of the urine, gastric fluid, saliva, and pancreatic secretion; in the electrical organs of the torpedo, and in large quantities in the blood of the higher forms of Leucocythæmia.[5] It has been shown by Diakonow [6] and Strecker [7] that lecithin decomposes on boiling with baryta-water into choline, glycero-phosphoric acid, and fatty acids, of which palmitic acid, stearic acid, and oleic acid have already been found. Hence it would appear that several different lecithins exist, of which *di-stearyl lecithin* has been prepared tolerably pure. From the analysis of this body Diakonow gives to it the formula $C_{44}H_{90}NPO_9$, whilst Strecker gave the formula $C_{42}H_{84}NPO_9$ to a lecithin which on decomposition yielded palmitic and oleic acids together with a little stearic acid.

[1] *Ann. Chim.* lxxx. 27, 60.
[2] *Ann. Chim. Phys.* [3], ii. 474.
[3] *Ib.* l. 172.
[4] *Med. Chem. Unters.* 216.
[5] *Ib.* 1866-71.
[6] *Ib.* ii. 221; iii. 405.
[7] *Ann. Chem. Pharm.* cxlviii. 77.

The following formulæ represent the chemical constitution of di-stearyl-lecithin:



*Preparation.*—In order to prepare lecithin, yolk of egg is shaken up with ether until this ceases to be coloured, the residue treated with water, quickly washed on a filter, and then digested with alcohol at 50°—60°. The solution is quickly evaporated down to a syrupy consistency, dissolved in a small quantity of absolute alcohol, and the filtered solution cooled in a freezing mixture. After some time stearin-lecithin separates out in nodular masses or less frequently in fine crystalline tablets, whilst oleïn-lecithin remains in solution. On drying the former compound remains as a wax-like, imperfectly-crystalline mass, which is very hygroscopic, and dissolves easily in ether-chloroform and the fatty oils. When the ethereal solution of this mass is shaken up with dilute sulphuric acid the latter substance extracts choline, and the ether contains *distearylglycerol-phosphoric acid*, $C_3H_5(C_{18}H_{35}O_2)_2PO_4H_2$. The potassium salt of this acid is a crystalline body (Diakonow).

Strecker also prepared his lecithin from yolk of egg, extracting it with a mixture of ether and alcohol, distilling off the ether, and adding alcohol to the residue in order to precipitate the fatty oils contained in the egg. On addition to the filtrate of an alcoholic solution of platinic chloride containing hydrochloric acid a flocculent, yellow precipitate was thrown down, which was purified by repeated solution in ether and precipitation with alcohol. Analysis then gave the formula $(C_{42}H_{83}PNO_8Cl)_2PtCl_4$. On passing sulphuretted hydrogen into the ethereal solution it was decomposed, and after evaporation of the hydrochloric acid the lecithin remained as a wax-like mass. The solution of this in alcohol-ether, on being shaken with silver oxide, lost its hydrochloric acid, silver oxide however being dissolved, which was removed by sulphuretted hydrogen. On evaporating, the lecithin remained as a homogeneous, translucent mass.

This body and its compounds are very easily decomposed. When an ethereal solution of the platinum salt is allowed to

stand, choline, platinum chloride separates out gradually, and the alcoholic solution of the hydrochloride of lecithin decomposes after some time with separation of fatty acids. The solution of free lecithin decomposes slowly in the cold but quickly on heating. Lecithin when brought into contact with water increases in bulk and the starch-like mass exhibits under the microscope various forms of filaments, spherules and drops.

Similar gelatinous forms were first observed by Virchow when nerve fibres are exposed to the action of water for some length of time, and are known as myeline forms.

712 *Protagon*, $C_{160}H_{308}N_5PO_{35}$. This very complicated compound must be mentioned here because it was formerly confounded with lecithin and was afterwards regarded as being a mixture of this body with cerebrin, a phosphoretted substance contained in the brain. Protagon (*πρωταγος* leading the van) was first discovered by Liebreich, who gave to it the formula $C_{116}H_{241}N_4PO_{22}$.[1] Its existence was afterwards corroborated by Gamgee and Blankenhorn, who assigned to it the above composition, remarking, however, that a definite formula can only be obtained from an examination of its decomposition-products.

The highest percentage of phosphorus found in this body by Liebreich was 1·5. Gamgee and Blankenhorn, who prepared the substance with great care and determined the phosphorus with accuracy, found, on the other hand, as a mean of five well agreeing analyses, the number 1·068.[2]

In order to prepare protagon, perfectly fresh ox brains are freed, as completely as possible, from blood and adhering membrane, and are then digested for many hours (18—24) in 85 per cent. alcohol in a large incubator kept constantly at 45°. The fluid is filtered whilst hot and the insoluble matter again treated with a fresh mixture of spirit, the proceeding being repeated four or five times, as long in fact as the filtrate cooled to 0° deposits a fair quantity of a white flocculent precipitate. This precipitate is collected on a filter, and being thence transferred to a stoppered bottle is thoroughly and repeatedly agitated with ether in order to dissolve cholesterin and other bodies soluble in ether. The ether having been removed first by decantation and then by filtration, the substance left undissolved is first of all dried between sheets of filter-paper in air and afterwards over sulphuric acid or phosphorus pentoxide. The resulting mass,

[1] *Ann. Chem. Pharm.* cxxxiv. 29.
[2] *Proc. Roy. Soc.* xxix. 151; xxx. 111.

which is snow-white, is reduced to powder, moistened with a little water and digested for many hours with alcohol heated to 45°. From the filtered liquid, if this be allowed to cool very gradually, the protagon separates in the form of microscopic needles mostly arranged in rosettes, the appearance and arrangement of which differ somewhat, as Liebreich has very exactly pointed out, according to the degree of concentration of the solution.

The once crystallised protagon thus obtained is collected on a filter, washed with ether, and dried first of all in air and ultimately over phosphorus pentoxide. It is then recrystallised as many times as required, the process always beginning by pulverizing and thoroughly shaking with cold ether.[1]

Like lecithin, protagon produces with water myeline forms, and like this it is also very easily decomposed; and amongst its products of decomposition Liebreich noticed choline, fatty acids, and glycerol-phosphoric acid.

## SULPHUR COMPOUNDS OF PROPENYL.

713 *Propenyl Hydrosulphides* or *Sulphhydrins* are formed by the action of the chlorhydrins on an alcoholic solution of potassium hydrosulphide.[2]

*Monosulphhydrin*, $C_3H_5(OH)_2SH$, is a thick, colourless liquid which possesses, when warmed, a peculiar disagreeable smell. It is scarcely soluble in water and forms amorphous mercaptides.

*Disulphhydrin*, $C_3H_5OH(SH)_2$, is a liquid similar to the above and contains two atoms of hydrogen easily replaceable by metals.

*Trisulphhydrin*, $C_3H_5(SH)_3$, is a colourless liquid much more mobile than glycerol and possessing an unpleasant, ethereal smell. The salts of the heavy metals yield flocculent precipitates with its alcoholic solution.

*Propenyl Monosulphonic Acid*, $C_3H_5(OH)_2SO_3H$, it obtained by oxidizing monosulphhydrin with nitric acid. It is a gum-like, deliquescent mass, whose salts crystallize with difficulty (Carius).

*Propenyl Disulphonic Acid*, $C_3H_5OH(SO_3H)_2$. The potassium salt is easily formed when a concentrated solution of normal

[1] Gamgee, *Physiological Chemistry of the Animal Body*, vol. i. 427.
[2] Carius and Ferrein, *Ann. Chem. Pharm.* cxxii. 71; Carius, *ib.* cxxiv. 221.

potassium sulphite is boiled with dichlorhydrin[1] or epichlorhydrin.[2] It forms large rhombic crystals having the formula $C_3H_6O(SO_3K)_2+2H_2O$. When its concentrated solution is treated with barium chloride the barium salt, $C_3H_6O(SO_3)_2Ba+2H_2O$, separates out, on standing, in warty concretions. If this be decomposed with sulphuric acid and neutralized with lead carbonate, the lead salt, $C_3H_6O(SO_3)_2Pb+2H_2O$, is obtained, crystallizing in large, easily-soluble crystals. By the action of sulphurreted hydrogen on the lead salt the free acid is obtained as a hygroscopic syrup.

*Propenyl Trisulphonic Acid*, $C_3H_5(SO_3H)_3$. When trichlorhydrin is boiled with a solution of potassium sulphite, it gradually dissolves, and on evaporation an imperfectly crystalline mass separates. This contains chlorine, and is probably a double salt of potassium chloride and potassium propenyl trisulphonate, and it is not decomposed into its constituents by recrystallization. When heated with sulphuric acid in order to drive off the hydrochloric acid and neutralized with barium carbonate, *barium propenyl trisulphonate*, $(C_3H_5)_2(SO_3)_6Ba_3$, is deposited as a difficultly-soluble powder (Schaüffelen).

*Chlorhydrin Sulphonic Acid*, $C_3H_5Cl(OH)SO_3H$, is formed by heating epichlorhydrin with acid sodium sulphite. The sodium salt, $C_3H_5Cl(OH)SO_3Na + 2H_2O$, thus obtained forms large, monoclinic crystals. The free acid is obtained by decomposing the alcoholic solution of the sodium salt with oxalic acid. It is a deliquescent syrup which forms salts usually crystallizing well.[3] When the sodium salt is heated with sodium sulphite, sodium propenyl disulphonate is formed (Paschke).

## NITROGEN COMPOUNDS OF PROPENY

714 *Propenyl Hydroxydiamine* or *Diamidohydrin*, $C_3H_5(NH_2)_2OH$. This body is formed, together with *glycidamine*, $C_3H_5(NH_2)O$, when dichlorhydrin is heated with a one-per-cent. solution of alcoholic ammonia. When the solution is evaporated the hydrochloride of the first base is formed. In order to separate it, the liquid is allowed to stand over ether until the free

[1] Schaüffelen, *Ann. Chem. Pharm.* cxlviii. 111.
[2] Paschke, *Journ. Prakt. Chem.* [2], i. 82.
[3] Darmstädter, *Ann. Chem. Pharm.* cxlviii. 125.

ammonia has disappeared. If more ether be gradually added, a small quantity of sal-ammoniac is first thrown down, then hydrochloride of diamidohydrin, and lastly the glycidamine salt, which crystallizes in needles or prisms if the materials are anhydrous; otherwise it is formed as a syrup, as it is excessively hygroscopic.

If dichlorhydrin be heated with strong alcoholic ammonia, *chlorhydrinimide*, $C_{12}H_{27}N_3ClO_4$, is formed, a white amorphous mass which swells up with water to form a voluminous jelly.[1]

*Propenyl Triamine*, $C_3H_5(NH_2)_3$, is obtained by the reduction of the corresponding nitro-compound, to be described hereafter. It is an oily, unpleasantly-smelling liquid, the hydrochloride forming a white crust and yielding a platinichloride crystallizing in octohedrons.

*Propenyl Trimethyl Ammonium Chloride*, $N(CH_3)_3C_3H_5(OH)_2Cl$, is formed by heating chlorhydrin with trimethylamine. It is deposited in needles easily soluble in water and its platinichloride crystallizes in orange-red, rectangular tables.[2]

*Trinitropropane*, $C_3H_5(NO_2)_3$, is formed by the action of silver nitrite on tribromhydrin. It is a heavy, yellow oil, boiling between 190° and 200°, and yielding with alcoholic potash the compound $C_3H_2K_3(NO_2)_3$ which is a white powder soluble in water.[3]

## GLYCERIC ACID, or DIOXYPROPIONIC ACID, $C_3H_6O_4$.

715 This substance was obtained by Debus[4] and Sokolow,[5] by oxidizing glycerol with nitric acid. It is also formed when glycerol is heated with bromine and water, or when calcium chlorlactate is treated in aqueous solution with silver oxide:[6]

$$\left.\begin{matrix} ClCH_2.CH(OH)CO_2 \\ ClCH_2.CH(OH)CO_2 \end{matrix}\right\rangle Ca + Ag_2O + H_2O =$$

$$\left.\begin{matrix} (OH)CH_2.CH(OH)CO_2 \\ (OH)CH_2.CH(OH)CO_2 \end{matrix}\right\rangle Ca + 2AgCl.$$

[1] Claus, *Ann. Chem. Pharm.* clxviii. 29.
[2] V. Meyer, *Ber. Deutsch. Chem. Ges.* ii. 186; Hanriot, *Ann. Chim. Phys.* [5], xvii. 99.
[3] Brackebusch, *Ber. Deutsch. Chem. Ges.* vi. 1289.
[4] *Ann. Chem. Pharm.* cvi. 79; cix. 227.
[5] *Ib.* cvi. 95.
[6] Frank, *Ib.* ccvi. 338.

In order to prepare glyceric acid a long cylinder is filled with equal parts of nitric acid, glycerol, and water, and the reaction which takes place after some little time is allowed to go on without the aid of heat. The product of this reaction is concentrated on a water-bath and then converted into the calcium salt (Debus) or lead salt,[1] from which, by means of oxalic acid or sulphuretted hydrogen, as the case may be, the free acid is separated. This remains, on evaporating the solution, as a strongly-acid syrup, which on standing deposits small needles of the anhydride $C_3H_4O_3$, whose molecular formula is doubtless a multiple of this. This is difficultly soluble, even in boiling water, and crystallizes from it in thin six-sided prisms. Boiling water converts this anhydride only slowly into glyceric acid, and this takes place more quickly in presence of a small quantity of milk of lime.[2] On dry distillation, water, formic acid, acetic acid, and pyroracemic acid are first given off;[3] and then pyrotartaric acid, its anhydride and other poducts.[4]

When distilled with acid potassium sulphate, pyroracemic acid is formed in large quantity:[5]

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CO_2H \end{array} + H_2O.$$

Glyceric acid is monobasic, and forms salts which usually crystallize well.

*Calcium Glycerate*, $(C_3H_5O_4)_2Ca + 2H_2O$, is deposited in crusts tolerably soluble in water. *Strontium Glycerate*, $(C_3H_5O_4)_2Sr$, is almost insoluble in cold water, but dissolves readily in hot water, and deposits in crystals united in warty concretions. *Lead Glycerate*, $(C_3H_5O_4)_2Pb$, is difficultly soluble in cold, but readily soluble in hot water, and crystallizes in hard crusts.

716 *Ethyl Glycerate*, $C_3H_5O_4(C_2H_5)$, is formed when glyceric acid is heated for some hours to 170°—190° with four times its bulk of absolute alcohol. It is a thick liquid having a bitter taste, and

[1] Beilstein, *Ann. Chem. Pharm.* cxx. 226; Mulder, *Ber. Deutsch. Chem. Ges.* ix. 1902.
[2] Sokolow, *Ib.* xi. 679.
[3] Moldenhauer, *Ann. Chem. Pharm.* cxxxi. 323.
[4] Böttinger, *ib.* cxcvi. 92.
[5] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiv. 320.

boiling between 230°—240°. By the action of nitro-sulphuric acid it is converted into the nitrate, $C_2H_3(NO_3)_2CO_2.C_2H_5$, a heavy, oily, easily-combustible liquid.[1]

*β-Dichlorpropionic Acid*, $CH_2Cl.CHCl.CO_2H$, is formed by oxidizing the corresponding chlorhydrin, and its chloride is obtained by the action of phosphorus chloride on glycerol. It crystallizes in small needles, melts at 50°, and boils with decomposition at 210°. On acting with absolute alcohol upon the chloride *ethyl β-dichlorpropionate*, $C_3H_3Cl_2O_2(C_2H_5)$, is formed, a liquid boiling at 183°—184°.

*β-Dibrompropionic Acid*, $CH_2Br.CHBr.CO_2H$, is obtained by oxidizing β-propenyl dibromhydrin with nitric acid,[2] and it is also formed when *a*-dibrompropionic acid is heated to 100° for eight days with fuming hydrobromic acid.[3] It is tolerably soluble in water, and crystallizes in two forms which can be produced at pleasure by bringing the fused acid in contact with the one or the other. The more stable form crystallizes in tables, which melt at 64°. Heated to a higher point, the second modification is formed, and this melts at 51°; it forms compact prisms, which when kept, pass into the first form.[4] Both modifications belong to the monoclinic system.[5] The salts of the acid are but slightly stable, and are easily converted, with formation of a metallic bromide, into bromacrylic acid.

*Amidoglycerol* or *Serin*, $C_2H_3(OH)(NH_2)CO_2H$, is formed by boiling serecin or silk-substance with dilute sulphuric acid. It crystallizes from hot water in hard oblique prisms having a faint sweet taste. In its chemical relations it agrees with the other amido-acids; it yields glyceric acid on treatment with nitrous acid.[6]

## BUTENYL ALCOHOL, $C_4H_7(OH)_3$.

717 It has already been stated (p. 166) that acetaldehyde is converted, with loss of water, into crotonaldehyde, and that this unites with hydrogen to form crotonyl alcohol, $CH_3.CH=CH.CH_2.OH_1$, butyraldehyde and normal butyl alcohol also

[1] Henry, *Ber. Deutsch. Chem. Ges.* iv. 705.
[2] Münder and Tollens, *Ann. Chem. Pharm.* clxvii. 222.
[3] Phillipi and Tollens, *ib.* clxxi. 337.
[4] Linnemann and Penl, *Ber. Deutsch. Chem. Ges.* viii. 1099; Tollens, *ib.* 1448, 1452.
[5] Zepharovich, *Jahresb. Chem.* 1878, 693.
[6] Cramer, *Jahresb.* 1865, 655.

being formed. The crotonaldehyde, which will be described later on, combines with a molecule of bromine to form *butenyl dibromhydrin*, $CH_3.CHBr.CHBr.CH_2OH$, and this when heated with a large quantity of water is converted into *butenyl-glycerol*, $CH_3.CH(OH).CH(OH).CH_2OH$. This is a thick, sweetish-tasting liquid, which boils under a diminished pressure of 27 mm. at 172°—175°. When heated with acetic anhydride to 150° the *triacetin*, $C_4H_7(C_2H_3O_2)_3$, is formed, a somewhat thick liquid, having a weak but pleasant smell, and boiling at 261°·8. When butenyl alcohol is heated with hydriodic acid it is reduced to secondary butyl iodide.[1]

## PENTENYL ALCOHOL, $C_5H_9(OH)_3$.

718 This is obtained from tiglic aldehyde, $C_5H_8O$, and forms a sweet-tasting syrup.[2]

## HEXENYL ALCOHOL, $C_6H_{11}(OH)_3$.

719 The point of departure for this glycerol is crotonyl methyl carbinol, $CH_2{=}CH.CH_2CH_2CH(OH)CH_3$, a body which will be described hereafter. The acetic ether of this carbinol combines with a molecule of bromine, and the product heated with acetic acid and silver acetate to 120° yields the triacetin, a thick liquid boiling at 280°—285°. This when boiled with water and lead oxide yields a glycerol possessing the following constitution, $HO.CH_2.CH(OH).CH_2.CH_2.CH(OH).CH_3$. It is a very thick liquid, having a sweetish-bitter taste, and boiling under a pressure of 10 mm. at 181°.[3]

[1] Lieben and Zeisel, *Monatsh. Chem.* i. 818.
[2] Herzig, *Monatsh. Chem.* iii. 118.
[3] Markownikow and Kablukow, *Ber. Deutsch. Chem. Ges.* xiii. 1842; xiv. 1711.

## COMPOUNDS OF THE MONAD ALCOHOL RADICALS, $C_nH_{2n-1}$, AND OF THE ACID RADICALS, $C_nH_{2n-3}O$.

720 The triad radicals can also act as monad radicals when two atoms of carbon are linked together by two combining units. Hence the compounds of these radicals stand to the olefines in the same relation as the monad radicals of the fatty acids do to the paraffins. Like the olefines, these hydrocarbons combine directly with the elements of the chlorine group, with their hydracids and so forth. Their compounds may be classed as primary, secondary, and tertiary.

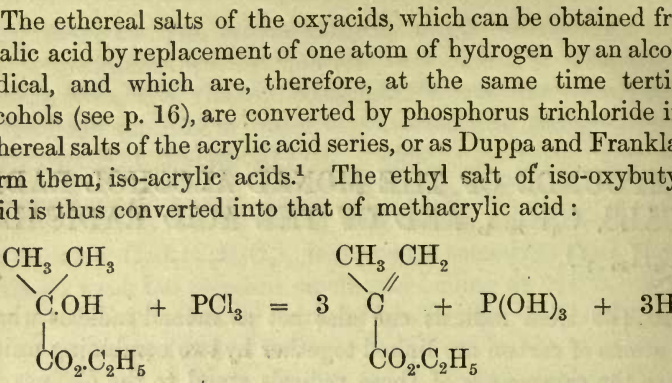
The first of these classes contains aldehydes and monobasic acids. Of these several occur in nature partly as glycerides in a variety of fats, whilst many of them can be artificially prepared. This group of acids is termed, from its first member, the *Acrylic Series.* The members of this series may be obtained by the action of alkalis, silver oxide, or lead oxide on the monosubstituted fatty acid; thus $\beta$-iodopropionic acid yields acrylic acid:

$$\begin{array}{l} CH_2I \\ | \\ CH_2 \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_2 \\ || \\ CH \\ | \\ CO_2H \end{array} + HI.$$

The oxyacids in which the hydroxyl is not attached to the carbon next to carboxyl, decompose on distillation into water and an acid of this group. Thus $\beta$-oxybutyric acid yields crotonic acid:

$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2 \\ | \\ CO_2H \end{array} = \begin{array}{l} CH_3 \\ | \\ CH \\ || \\ CH \\ | \\ CO_2H \end{array} + H_2O.$$

The ethereal salts of the oxyacids, which can be obtained from oxalic acid by replacement of one atom of hydrogen by an alcohol radical, and which are, therefore, at the same time tertiary alcohols (see p. 16), are converted by phosphorus trichloride into ethereal salts of the acrylic acid series, or as Duppa and Frankland term them, iso-acrylic acids.[1] The ethyl salt of iso-oxybutyric acid is thus converted into that of methacrylic acid:

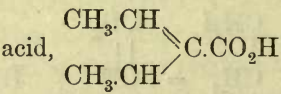


On fusion with caustic potash the acids of this group are decomposed into two molecules of a fatty acid, inasmuch as the molecule splits up at the point of double linkage; thus crotonic acid decomposes into two molecules of acetic acid:

$$CH_3.CH{=}CH.CO_2H + 2KOH = 2CH_3.CO_2K + H_2.$$

The constitution of these acids may in many cases be ascertained by this reaction, though not in all cases, as isomeric acids may yield the same products of decomposition. Thus, for instance, the two following acids, having the formula $C_6H_{10}O_2$, yield normal butyric and acetic acids:

Hydrosorbic acid, $CH_3.CH{=}CH.CH_2.CH_2.CO_2H$

Ethyl-crotonic acid, 

In addition to this, many of these acids are converted by heating into isomeric modifications. For example, isocrotonic acid, $CH_2{=}CH.CH_2.CO_2H$, is thus converted into crotonic acid, and therefore, when fused with caustic potash yields only acetic acid.

In their physical characters these acids resemble the group of the fatty acids. The first terms of the series are miscible with water and easily volatile. With increase of molecular weight the solubility in water diminishes and the boiling-point increases. The higher members of the series are oily liquids at the ordinary temperature and not volatile without decomposition, and these when acted upon with even a small quantity of nitric

[1] *Journ. Chem. Soc.* xviii. 133.

acid are converted into crystalline isomeric modifications. Their glycerides exhibit similar properties. They are distinguished from the corresponding fatty acids, inasmuch as their lead salts are easily soluble in ether, and by this means they can be readily separated from the latter series with which they occur.

721 The secondary and tertiary alcohols belonging to this series are obtained by reactions similar to those employed for the preparation of the corresponding compounds of the fatty group. The members already known are described on p. 411.

## THE ALLYL COMPOUNDS.

722 In 1844 Wertheim proved that the chief constituent of oil of garlic obtained from the bulbs of *Allium sativum* is the sulphide of a radical to which he gave the name of *Allyl*, $C_3H_5$.[1] At the same time Will showed that the volatile oil of mustard (*Sinapis nigra*) may be looked upon as the sulphocyanide of the same radical,[2] and Wertheim then made the interesting observation that by distilling the roots of garlic mustard (*Alliaria officinalis*), a plant which, like the mustard plant, is a crucifer, the volatile oil of mustard can be obtained, whilst the leaves of the plant yield a volatile body which smells exactly like garlic oil.[3] Shortly after he showed that garlic oil can be converted into mustard oil, and *vice versâ*.[4]

By the action of iodide of phosphorus on glycerol, Berthelot and de Luca in 1854 obtained the compound $C_3H_5I$, to which they gave the name of iodopropylene,[5] and they, as well as Zinin,[6] found that this body can be converted into mustard oil by heating it with potassium thiocyanate or silver thiocyanate.[7] Other allyl compounds were then prepared by these chemists,[8] as well as by Hofmann and Cahours.[9]

*Allyl Alcohol*, $C_3H_5.OH$. Cahours and Hofmann obtained this body by treating the iodide with silver oxalate, and then passing dry ammonia into the allyl oxalate, when oxamide separates out rapidly :

$$(C_3H_5O)_2C_2O_2 + 2NH_3 = 2C_3H_5.OH + C_2O_2\,(NH_2)_2.$$

[1] *Ann. Chem. Pharm.* li. 289.
[2] *Ib.* lii. 1.
[3] *Ib.* lii. 52.
[4] *Ib.* lv. 297.
[5] *Ib.* xcii. 307.
[6] *Ib.* xcv. 128.
[7] *Ib.* xcvii. 126.
[8] *Ib.* c. 359.
[9] *Ib.* c. 355 ; cii. 285.

The allyl alcohol is then distilled off by heating in a bath of chloride of calcium.

Allyl iodide can also be converted into the alcohol by the methods already described (Part I. p. 154). The simplest plan is, however, to heat glycerol with oxalic acid, when monoformin (p. 365) is obtained, and this decomposes as follows:

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2O.COH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2.OH \end{array} + CO_2 + H_2O.$$

For this purpose 4 parts of glycerol and 1 part of crystallized oxalic acid are heated in a retort to 195°, the receiver changed, and the temperature allowed to rise to 260°. The distillate is rectified, warmed with caustic potash, re-distilled, and dried, first over caustic potash, and finally over caustic baryta. If the oxalic acid contain alkali, as is almost always the case, from half to one per cent. of sal-ammoniac must be added in order to get a good yield.[1]

Allyl alcohol is also found in small quantity in crude wood-spirit.[2]

It is a mobile liquid which possesses a pungent odour, boils at 96°·6, and at 0° has a specific gravity of 0·8706 (Thorpe). It retains water very strongly, and when mixed with this liquid the boiling-point is lowered.[3] When heated with solid caustic potash to 150°, propyl alcohol is formed together with ethyl alcohol, formic acid, propionic acid, and other compounds.[4] Chromic acid solution oxidizes it to acryl aldehyde, formic acid also being produced.[5]

Its compounds with the halogens and their hydracids have already been described. These may be looked upon as propenyl compounds, or as substitution-products of primary propyl alcohol.

[1] Tollens, *Ann. Chem. Pharm.* clvi. 129.
[2] Aronheim, *Ber. Deutsch. Chem. Ges.* vii. 1381; Grodski and Kärmer, *ib.* vii. 1492.
[3] Dittmar and Stewart, *Chem. News*, xxxiii. 53.
[4] Tollens, *Ann. Chem. Pharm.* clix. 92.
[5] Rinne and Tollens, *ib.* clix. 110.

## ALLYL ETHERS.

723 *Allyl Oxide* or *Di-allyl Ether*, $(C_3H_5)_2O$, was obtained by Berthelot and de Luca, by acting with mercuric oxide on allyl iodide,[1] and Cahours and Hofmann also obtained it by the same method, as well as by dissolving sodium in allyl alcohol, and treating the product with allyl iodide.[2] It is a liquid smelling like horse-radish, and boils at 82°.

*Ethyl Allyl Ether*, $C_3H_5O(C_2H_5)$, boils at 66°—67°, and has a specific gravity of 0·7651 at 20° (Brühl).

## ETHEREAL SALTS OF ALLYL

724 *Allyl Chloride*, $C_3H_5Cl$, is obtained by heating the iodide with mercuric chloride, or by warming the oxalate with calcium chloride and alcohol at 100°.[3] It is, however, best obtained by the action of phosphorus trichloride on the alcohol.[4] It is a liquid possessing a pungent smell, boiling at 44°·6, and at 0° having a specific gravity of 0·9547. It combines with hypochlorous acid to form β-dichlorhydrin.

*Allyl Bromide*, $C_3H_5Br$. This compound, which serves for the preparation of the trimethylene compounds, is best obtained by pouring a mixture of equal volumes of sulphuric acid and water on to potassium bromide, and dropping allyl alcohol into the warmed mixture.[5] It is a pungently smelling liquid, having at 0° a specific gravity of 1·461, and boiling at 70°—71° (Tollens).

These two ethereal salts of allyl unite with chlorine or bromine to form propenyl compounds, and with the hydracids, according to the conditions, to form propylene or trimethylene compounds.

*Allyl Iodide*, $C_3H_5I$. In order to prepare this, 160 parts of allyl alcohol are mixed with 254 parts of iodine and twenty parts of phosphorus, and the mixture, after standing twenty-four hours, is distilled in a stream of carbon dioxide (Tollens and Henninger).

[1] *Ann. Chim. Phys.* [3]; xlviii. 286.
[2] *Ann. Chem. Pharm.* cii. 285.
[3] Oppenheim. *Ib.* cxl. 205.
[4] Tollens and Henninger, *Ib.* clvi. 154.
[5] Grosheintz, *Bull. Soc. Chim.* xxx. 98.

To prepare it from glycerol, fifteen parts of this liquid, which must be well dried, are mixed with ten parts of iodine in a retort, and three parts of white phosphorus gradually added, the mixture being then distilled in an atmosphere of carbon dioxide.[1] The product thus obtained usually contains secondary propyl iodide and allyl alcohol (p. 358). In order to purify it, it is dissolved in alcohol and shaken up with mercury, by which means *allyl mercury iodide*, $C_3H_5HgI$, is formed, and this is crystallized out from boiling alcohol, and then decomposed by water and the theoretical quantity of iodine.[2]

Allyl iodide is a liquid having a pungent alliaceous smell, boiling at 101°·5—102°, and having at 12° a specific gravity of 1·848. When heated with 20 parts of water to 100°, it gradually dissolves with formation of allyl alcohol.[3] Bromine converts it into tribromhydrin.

The above-mentioned mercury compound crystallizes in white scales, and is converted by moist silver oxide into *allyl mercury hydroxide*, $C_3H_5Hg(OH)$, which is a syrupy alkaline liquid, forming salts with acids.[4]

If allyl iodide be added to an alcoholic solution of potassium nitro-ethane, allyl-nitro-ethane, $C_5H_9NO_2$, is formed. This is volatile not without decomposition, and it is converted by zinc and hydrochloric acid into the amine, $C_5H_9NH_2$, boiling at 85°.[5]

725 *Allyl Nitrate*, $C_3H_5NO_3$, is formed by the action of silver nitrate on allyl bromide. It is a pungent mobile liquid boiling at 106°.[6]

*Allyl Borate*, $(C_3H_5)_3BO_3$, is formed by heating allyl alcohol with boron trioxide to 130°. It is a liquid giving a pungent vapour which causes a flow of tears, and boils at 168°—175°. It combines with six atoms of bromine to form a thick liquid, which is decomposed by water into boric acid and $\beta$-dibromhydrin.[7]

*Allyl Formate*, $C_3H_5CHO_2$, is formed in the preparation of formic acid from glycerol and oxalic acid. It is a liquid possessing a sharp mustard-like smell, and boiling at 82°—83°.[8]

[1] Kannonikow and Saytzew, *Ann. Chem Pharm.* clxxxv. 191.
[2] Linnemann, *ib.* Suppl. iii. 263.
[3] Niederist, *Ann. Chem. Pharm.* cxcvi. 350.
[4] Krasowsky, *Zeitsch. Chem.* 1870, 527.
[5] Gal, *Bull. Soc. Chim.* [2], xx. 13.
[6] Henry, *Ber. Deutsch. Chem. Ges.* v. 452.
[7] Councler, *Journ. Prakt. Chem* [2], xviii. 376.
[8] Tollens, *Zeitsch. Chem.* 1866, 518; 1868, 441.

*Allyl Acetate*, $C_3H_5.C_2H_3O$, is an aromatic pungent-smelling liquid, having a sharp taste, and boiling at 103°—104°.[1]

*Allyl Oxalate*, $(C_3H_5)_2C_2O_4$, is an oily liquid which has a smell resembling both mustard and ethyl oxalate, and boils at 207° (Cahours and Hofmann).

*Allyl Cyanformate*, $C_3H_5.O.CO.CN$. Cyanogen gas is absorbed by allyl alcohol with evolution of heat, the compound $C_3H_5(CN)_2OH$ being formed. This is a colourless liquid, smelling like acetonitril, and boiling at 150°—151°.[2] It is decomposed by fuming hydrochloric acid with formation of sal-ammoniac, oxamide, allyl chloride, and allyl cyanformate. This last is a liquid having a mustard-like smell, and boiling at 135°.[3]

726 *Substitution products of Allyl Alcohol and of its Ethers and Ethereal Salts.* The ethers are obtained by the action of alcoholic potash on the isomeric epichlorhydrins or epibromhydrins, and the ethereal salts are produced when the latter compounds are treated with potassium acetate, silver nitrate, &c., whilst the alcohols can be obtained from the ethereal salts. It is usual to distinguish as *a*-compounds those containing the group $CH_2 = CX.CH_2$ and as *β*-compounds those containing the group $CHX = CH.CH_2$, in which X signifies a halogen.

| | | B.P. |
|---|---|---|
| [4] *β*-bromallyl alcohol, | $C_3H_4Br.OH$ | 155° |
| [5] *a*-chlorallyl ethyl ether, | $\left.\begin{matrix}C_3H_4Cl\\C_2H_5\end{matrix}\right\}O$ | 110° |
| [6] *β*-chlorallyl ethyl ether, | $\left.\begin{matrix}C_3H_4Cl\\C_2H_5\end{matrix}\right\}O$ | 120°—125° |
| [7] *a*-bromallyl ethyl ether, | $\left.\begin{matrix}C_3H_4Br\\C_2H_5\end{matrix}\right\}O$ | 130°—135° |
| [8] *β*-bromallyl ether, | $(C_3H_4Br)_2O$ | 212°—215° |
| [4] *β*-bromallyl nitrate, | $C_3H_4Br.NO_3$ | 140°—150° |
| [4] *a*-chlorallyl acetate, | $C_3H_4Cl(C_2H_3O_2)$ | 140°—145° |
| [4] *β*-chlorallyl acetate, | $C_3H_4Cl(C_2H_3O_2)$ | 156°—159° |

*Iodallyl Alcohol*, $C_3H_4I.OH$, is formed by the action of a dilute solution of carbonate of soda on *β*-propenyl di-iodhydrate, and it crystallizes in needles which melt at 160°.[9]

[1] Zinin, *Ann. Chem. Pharm.* xcvi. 361; Cahours and Hofmann, *loc cit.*; Brühl *Liebig's Ann.* cc. 179. [2] Tollens, *Ber. Deutsch. Chem. Ges.* v. 621.
[3] Wagner and Tollens, *ib.* v. 1045.
[4] Henry, *Ber. Deutsch. Chem. Ges.* v. 449. [5] *Ib.* v. 189.
[6] Friedel and Silva, *Jahresb.* 1872, 224.
[7] Henry, *Ber. Deutsch. Chem. Ges.* v. 188. [8] Henry, *ib.* vi. 729.
[9] Hübner and Lellmann, *ib.* xiii. 461.

## SULPHUR COMPOUNDS OF ALLYL.

727 *Allyl Hydrosulphide,* $C_3H_5.SH$. This mercaptan was first obtained by Cahours and Hofmann by the action of the iodide upon an alcoholic solution of potassium hydrosulphide. It is a liquid boiling at 90°, and possessing a smell resembling that of oil of garlic, though being somewhat more ethereal. It unites with mercuric oxide to form a mercaptide, which crystallizes from alcohol in pearly glistening scales.

*Allyl Sulphide,* $(C_3H_5)_2S$. Oil of garlic was first investigated by Cadet, and that of onions (*Allium lepa*) by Fourcroy and Vauquelin, and in this the latter chemists proved the presence of sulphur.[1] Wertheim then showed that the first of these oils consists principally of allyl sulphide, and Cahours and Hofmann obtained it artificially by the action of allyl iodide on an alcoholic solution of potassium sulphide. In addition to garlic, various other plants, as the herb and seeds of *Thlaspi arvense,*[2] *Iberis amara,* and other crucifers, yield allyl sulphide on distillation with water, together usually with oil of mustard.[3]

Both allyl sulphide and mustard-oil are products of decomposition of more complicated compounds. That which yields mustard-oil is known, but not that from which the allyl sulphide is derived. That this latter, for example, is not contained ready-formed in the seeds of *Thlaspi arvense* is shown by the fact that when they are bruised dry they are odourless, and that it is only when they are macerated and bruised in water that the smell becomes evident. Further particulars of this will be given under Mustard-oil.

Allyl sulphide is a powerfully refracting liquid, which does not possess so unpleasant a smell as the crude oil of garlic, and boils at 140°. If mixed with an alcoholic solution of silver nitrate, a precipitate of $(C_3H_5)_2S(AgNO_3)_2$ is thrown down, and this crystallizes from hot alcohol in needles. Precipitates are also produced with mercuric chloride, platinic chloride, &c.

The ethereal oil of assafœtida appears also to contain allyl sulphide, as its mercury compound yields mustard-oil on distillation with potassium thiocyanate.[4]

[1] Gmelin, *Handb. Chem.* ix. 372.
[2] Wertheim, *Ann. Chem. Pharm.* li. 289 ; lv. 297.
[3] Pless, *ib.* lviii. 36.
[4] Hlasiwetz, *Ann. Chem. Pharm.* lxxi. 23.

## NITROGEN BASES OF ALLYL.

728 *Allylamine*, $C_3H_5NH_2$, was prepared by Hofmann and Cahours from allyl isocyanate and from allyl iodide. It is best, however, prepared from mustard-oil by treating it with zinc and hydrochloric acid[1] or with sulphuric acid containing some water:[2]

$$N\begin{cases} C_3H_5 \\ CS \end{cases} + H_2O = N\begin{cases} C_3H_5 \\ H_2 \end{cases} + COS.$$

Allylamine is a liquid possessing a strong ammoniacal odour, and causing sneezing and a flow of tears. It boils at 58°, and has a specific gravity at 15° of 0·864. It is miscible with water with evolution of heat, and precipitates many metallic salts. The sulphate forms feathery crystals, and the hydrochloride is deposited in deliquescent needles, whilst the platinichloride forms orange-coloured monoclinic tablets.

*Triallylamine*, $(C_3H_5)_3N$, is obtained by distilling tetrallylammonium hydroxide (Cahours and Hofmann), or more simply by distilling the corresponding bromide with an excess of freshly fused caustic potash.[3] Its formation from allyl chloride and potassium cyanide is remarkable. If an alcoholic solution of these bodies be allowed to stand, the tertiary base is formed together with the nitril of ethoxybutyric acid, pyrotartaric acid and its nitril,[4] the following reactions taking place:

(1) $CH_2{=}CH.CH_2Cl + KCN + OH.C_2H_5 = CH_3.CH(OC_2H_5)CH_2.CN + KCl.$

(2) $CH_2{=}CH.CH_2Cl. + 2KCN + H_2O = CH_3.CH(CN)CH_2.CN + KCl + KOH.$

(3) $CH_3.CH(CN)CH_2.CN + 2KOH + 2H_2O = CH_3.CH(CO_2K)CH_2.CO_2K + 2NH_3.$

(4) $3C_3H_5Cl + 4NH_3 = (C_3H_5)_3N + 3NH_4Cl.$

Triallylamine is a light, unpleasantly pungent-smelling liquid, boiling at 150°—151°

[1] Oeser, *Ann. Chem. Pharm.* cxxxiv. 8.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* i. 182; Rinne, *Ann. Chem Pharm.* clxviii. 262.
[3] Grosheintz, *Bull. Soc. Chim.* xxxi. 391.
[4] Pinner, *Ber. Deutsch. Chem. Ges.* xii. 2054.

*Tetrallylammonium Iodide*, $N(C_3H_5)_4I$. This is the chief product of the action of ammonia on allyl iodide. Indeed, at ordinary temperatures crystals of this compound separate out, the quantity being increased by the addition of caustic potash as the salt is insoluble in concentrated caustic ley. Freshly precipitated silver oxide converts it into the strongly caustic and alkaline hydroxide.

729 *Mixed Allylamines.* The two following have been obtained by Rinne[1] by heating allylamine with ethyl iodide:

| | | B.P. |
|---|---|---|
| Ethyl allylamine, | $N\begin{cases} C_3H_5 \\ C_2H_5 \\ H \end{cases}$ | 84° |
| Diethyl allylamine, | $N\begin{cases} C_3H_5 \\ C_2H_5 \\ C_2H_5 \end{cases}$ | 100°—103° |

*Dimonochlorallylamine*, $(C_3H_4Cl)_2NH$, is formed by heating trichlorhydrin with alcoholic ammonia. It is an oily liquid which boils with decomposition at 194°, and possesses a characteristic smell and an alkaline reaction.[2]

Tribromhydrin yields a corresponding compound,[3] whilst *a*-tetrachlorglycid forms *tetrachlordiallylamine*, $(C_3H_3Cl_2)_2NH$, a strongly alkaline oily liquid which evaporates in a current of steam.[4]

## CYANOGEN COMPOUNDS OF ALLYL.

730 *Allyl Carbamine*, $CN.C_3H_5$, is obtained by heating allyl iodide with silver cyanide. It is a mobile liquid which boils between 96° and 106°. Its smell is so penetrating and unpleasant that when a bottle containing it is opened the air of the room is offensive for many days, and so much is this the case that it could not be carefully further examined.[5]

*Allyl Carbimide*, or *Allyl Isocyanate*, $CO.NC_3H_5$, was obtained by Cahours and Hofmann by acting with allyl iodide on silver

[1] *Ann. Chem. Pharm.* clxviii. 261.
[2] Engler, *Ann. Chem. Pharm.* cxlii. 77.
[3] Simpson, *Ann. Chim. Phys.* [3], lvi. 129; Reboul, *Ann. Chem. Pharm.* Suppl. i. 232.
[4] Fittig and Pfeffer, *Ann. Chem. Pharm.* cxxxv. 363.
[5] Lieke, *Ann. Chem. Pharm.* cxii. 316.

cyanate. It is an unpleasantly smelling liquid which causes a flow of tears and boils at 82°.

*Allyl Thiocyanate,* $NC.SC_3H_5$. As soon as oil of mustard had been artificially prepared by heating allyl iodide with potassium thiocyanate or silver thiocyanate, this oil was naturally looked upon as allyl thiocyanate. Further examination proved that it is not this compound but its isomeride, allyl thiocarbimide, and its formation by the above reaction, by which it must be remembered the other iodides of the alcohol radicals yield the true ethereal salts of thiocyanic acid, remained unexplained until Billeter[1] and Gerlich[2] showed that allyl thiocyanate possesses the remarkable property of being easily converted into the isomeric oil of mustard, whilst all the other ethereal salts of thiocyanic acid are very stable compounds. Billeter obtained the thiocyanate by the action of lead allyl mercaptide on an ethereal solution of cyanogen chloride:

$$(C_3H_5)_2S_2Pb + 2CNCl = 2C_3H_5.SCN + PbCl_2.$$

According to Gerlich it is obtained when a solution of ammonium thiocyanate in three parts of alcohol is mixed with allyl bromide, and the whole allowed to stand in a vessel surrounded by ice,[3] and, when the reaction is complete, precipitating with ice-cold water.

Allyl thiocyanate is a colourless, strong refracting, oily liquid possessing an alliaceous odour, at the same time reminding one of that of hydrocyanic acid. It appears to exert a poisonous action, inasmuch as on working with the substance for some time headache, nausea, and nervous excitement are noticed. It begins to boil at 161°, but the boiling-point soon sinks, and an intense smell of mustard-oil is evolved; the whole of the allyl thiocyanate being completely converted into this substance if an inverted condenser be employed, and the liquid heated until the boiling-point sinks to 148°—149°. This molecular interchange takes place slowly at the ordinary temperature. Alcoholic potash converts it into potassium thiocyanate and allyl mercaptan, and when brought in contact with sodium amalgam it is converted by a violent reaction into allyl carbamine.

731 *Allyl Thiocarbimide,* $CS.NC_3H_5$. The Attic Greek comedians mention mustard as a biting substance which causes a flow of tears, but is an excellent substance for giving a relish to

[1] *Ber. Deutsch. Chem. Ges.* viii. 464. [2] *Ib.* viii. 650.
[3] *Ann. Chem. Pharm.* clxxviii. 80.

certain kinds of food. That this well known property of mustard is due to the presence of a volatile oil appears to have been first observed by Lefebre in 1660. Boerhave also mentions the same fact in 1732, and Thibierge in 1819 proved that this oil contains sulphur,[1] whilst Boutron and Robiquet,[2] as well as Fauré,[3] found in 1831 that the mustard seeds do not contain it ready formed. Boutron and Fremy then showed that the mustard seeds contain a peculiar albuminoid substance, which when brought in contact with the odourless aqueous extract obtained from mustard-flour, which has previously been treated with hot alcohol, brings about the formation of the volatile oil. Bussy next isolated the compound from which the mustard-oil is obtained by this decomposition, and found that it is the potassium salt of an acid to which he gave the name of myronic acid (*μύρον*, perfume or balsam) and that when placed in contact with water and with the above-named ferment, termed myrosin, it yields the essential oil.[5] Will and Körner investigated this subject more fully.

In place of common mustard seeds those of *Sinapis juncea* are much used. This kind of mustard is grown in India, Central Asia, and South Russia, and also yields oil of mustard, as also do horse-radish,[6] the roots of *Reseda odorata*,[7] and other plants which have been mentioned (p. 386).

In order to prepare mustard-oil the seeds, freed from fatty oil by pressure, are mixed with from 3 to 6 parts of water to form a paste, and then an aqueous extract of white mustard is added, this not yielding any mustard-oil, but being rich in myrosin. The water must be cold, as hot water coagulates myrosin, like albumen, and renders it inactive. After 24 hours the whole is distilled, the oil separated from the water, and the latter used for another preparation as it contains some dissolved oil. A thousand parts of black mustard seed macerated with fresh water yield from 2 to 7 parts of the oil, but if water saturated with the oil by previous distillations be used, the product may amount to from 11 to 12 parts.

Oil of mustard is now also artificially prepared by the action of potassium thiocyanate on allyl iodide at 50°—60°. This usually also contains the isomeric allyl thiocyanate.[8]

[1] *Journ. Pharm.* v. 439. [2] *Ib.* xvii. 294. [3] *Ib.* xvii. 299; xxi. 464.
[4] *Ib.* xxvi 468. [5] *Ib.* xxvi. 39.
[6] Hubatka, *Ann. Chem. Pharm.* xlvii. 153.
[7] Vollrath, *Jahresb.* 1871, 408.
[8] Billeter, *Ber. Deutsch. Chem. Ges.* viii. 820.

Wertheim found that the mercuric chloride compound of oil of garlic when heated with potassium thiocyanate to 120°—130° is converted into oil of mustard; and *vice versâ*, the latter is converted into oil of garlic when heated with potassium sulphide to 100°.

The composition of oil of mustard was first exactly determined by Will, who also completely investigated its derivatives.

*Properties.*—Oil of mustard is a colourless, highly-refracting liquid, boiling at 150°·7, and at 0° having a specific gravity of 1·036. Its taste and smell are penetrating and pungent, causing a flow of tears, and it produces blisters on the skin, for which reason it is used in medicine as an excitant. On exposure to light it gradually becomes yellow, depositing a deep-yellow amorphous powder which contains nitrogen and sulphur and closely resembles pseudosulphocyanogen (Vol. I., p. 674).

Robiquet and Bussy observed that when crude oil of mustard is heated for some time to 100° in a distillation-apparatus a light ethereal-smelling oil passes over.[1] This was shown by Will to be crotonitril, $C_3H_5.CN$. It is formed by the action of water on oil of mustard, this substance losing sulphur. It occurs in commercial oil of mustard in varying quantities which may amount to as much as 50 per cent.[2]

*Chlorallylthiocarbimide*, $CS.NC_3H_4Cl$, is formed by heating epichlorhydrin with potassium thiocyanate and alcohol. It is a very pungent-smelling liquid boiling at 185°. The corresponding bromine compound boils at 200°.[3]

## Myronic Acid, $C_{10}H_{19}NS_2O_{10}$.

732 This is scarcely known in the free state. Its potassium salt, as has been stated, is contained in the seeds of black mustard, and it was first obtained by Bussy. Other chemists did not succeed in preparing it, but its existence was corroborated by Ludwig and Lange,[4] and its formula ascertained by Will and Körner.[5]

In order to prepare potassium myronate, black mustard pulverised, but not freed from oil by pressure, is heated to the boiling-point with alcohol in order to render the myrosin inactive. The dried and pressed residue is then extracted with

[1] *Ann. Chim. Phys.* lxxii. 328.
[2] *Ann. Chem. Pharm.* cxxv. 278.
[3] Henry, *Ber. Deutsch. Chem. Ges.* v. 188.
[4] *Zeitsch. Pharm.* iii. 403 and 577.
[5] *Ann. Chem. Pharm.* cxxv. 257.

cold water and the extract treated with barium carbonate and evaporated on a water-bath, the residue extracted with alcohol and the solution thus obtained allowed to evaporate, when potassium myronate, $C_{10}H_{18}KNS_2O_{10}$, separates out. This is purified by recrystallization from strong boiling alcohol, when the salt separates out in silky needles, whilst from an aqueous solution, in which it is much more readily soluble, it is deposited in the form of short, glassy, four-sided prisms, which are odourless and have a cooling, bitter taste. When the concentrated solution is decomposed by tartaric acid and alcohol added, a solution of free myronic acid is obtained, but as yet the acid has not been prepared in the pure state.

Myronic acid is also found in the seeds of *Brassica rapa*, whilst it does not occur in those of *Brassica napus*. If the meal of the latter be rubbed up with water, a peculiar smell, different from that of mustard-oil, is noticed, from which the occurrence of another sulphur compound is rendered probable.[1]

When a solution of myrosin or an extract of white mustard is added to an aqueous solution of the potassium salt, this latter decomposes into oil of mustard, acid potassium sulphate, and glucose:

$$C_{10}H_{18}KNS_2O_{10} = C_4H_5NS + HKSO_4 + C_6H_{12}O_6.$$

At the same time a part of the oil is converted into sulphur and crotonitril.

When silver nitrate is added to a solution of potassium myronate a white precipitate of $C_4H_5NAg_2S_2O_4$ is thrown down and glucose remains in solution:

$$C_{10}H_{18}KNS_2O_{10} + 2AgNO_3 = C_4H_5NAg_2S_2O_4 + C_6H_{12}O_6 + KNO_3 + HNO_3.$$

The silver compound is decomposed on heating it with water into silver sulphate and oil of mustard:

$$C_4H_5NAg_2S_2O_4 = C_4H_5NS + Ag_2SO_4.$$

In this case silver sulphide and crotonitril are also formed, and these products are also obtained together with free sulphur and sulphuric acid by the action of sulphuretted hydrogen. The constitution of myronic acid is not known.

733 *Sinalbin*, $C_{30}H_{44}N_2S_2O_{16}$. This compound, which is contained in white mustard seed (*Sinapis alba*), may here be mentioned

[1] Ritthausen, *Journ. Prakt. Chem.* [2], xxiv. 273.

owing to its analogy to potassium myronate, although the products of decomposition which it yields belong to another group which will be afterwards described. It has long been known that powdered white mustard when rubbed up with water possesses a sharp taste but evolves no smell. The substance from which this sharp-tasting compound is produced was isolated by Robiquet and Boutron,[1] but more accurately examined by Will, who gave to it the above name and proposed that the corresponding potassium myronate should be termed *sinnigrin*.[2] This chemist, together with Laubenheimer, then investigated sinalbin more exactly.[3] In order to prepare it, the seeds, freed from the fatty oils by pressure, are dissolved in spirits of wine, and the crystalline mass which separates on cooling is dissolved in a small quantity of water. The filtered solution is precipitated by alcohol and the precipitate recrystallized from boiling spirit. Sinalbin is easily soluble in water, less so in alcohol, and crystallizes in small, pearly needles. Myrosin converts it in aqueous solution into sinalbin-mustard oil, acid sulphate of sinapine and glucose:

$$C_{30}H_{44}N_2S_2O_{16} = C_7H_7O.NCS + C_{16}H_{23}NO_5.H_2SO_4 + C_6H_{12}O_6.$$

Sinalbin-mustard-oil is an oily, non-volatile liquid, possessing an exceedingly sharp taste and producing blisters on the skin, though not acting so energetically as mustard-oil. As in the case with the latter compound it also easily loses sulphur, yielding the nitril of an oxyphenylacetic acid, $C_6H_4(OH)CH_2.CO_2H$.

## CARBAMIDE COMPOUNDS OF ALLYL.

734 *Allyl Urea*, $CO.N_2H_3(C_3H_5)$, is obtained by acting with aqueous ammonia on allyl carbimide[4] and also by boiling oxalylthiosinamine with a solution of silver nitrate.[5] It deposits in large prisms which are easily soluble in water and melt at 241°.

*Diallyl Urea*, $CO(NH.C_3H_5)_2$, was discovered in 1840 by Simon, who obtained it by acting with lead oxide and water on mustard oil, and termed it *sinapoline*. It was afterwards

[1] *Journ. Pharm.* xvii. 279.
[2] *Wien. Akad. Ber.* [2], lxi. 178.
[3] *Liebig's Ann.* cxcix. 150.
[4] Cahours and Hofmann, *Ann. Chem. Pharm.* cii. 290.
[5] Maly, *Zeitsch. Chem.* 1869, 261.

investigated by Will, who prepared it by boiling oil of mustard with baryta water:

$$N(CS)C_3H_5 + H_2O = N(CO)C_3H_5 + H_2S$$
$$2N(CO)C_3H_5 + H_2O = CO(NH.C_3H_5)_2 + CO_2.$$

Diallyl carbamide is also formed when allyl carbimide is heated with water (Cahours and Hofmann). It crystallizes from hot water in glistening saponaceous laminæ, which melt at 100°. It has an alkaline reaction and volatilizes in a current of steam.

*Allyl-thio-urea*, $CS.N_2H_3(C_3H_5)$, was obtained in 1834 by Dumas and Pelouze by the action of ammonia on oil of mustard. It was then examined by Will, who proposed for it the name of *thio-sinamine* in place of that which had been hitherto used, namely mustard-oil ammonia. In order to prepare it, oil of mustard is mixed with four volumes of aqueous ammonia, and ammonia gas passed in to saturation, when the thio-carbamide gradually crystallizes out. It forms glistening crystals which are tolerably soluble in water and easily soluble in alcohol, and melt at 74°. When given in moderate doses it produces palpitation and sleeplessness, ammonium thiocyanate being found in the urine.[1] It acts as a weak base and resembles the other carbamines in combining with salts. When bromine is added to its alcoholic solution the dibromide, $C_4H_8N_2SBr_2$, is formed. This crystallizes in six-sided prisms and contains one atom of bromine much more intimately united than the other. It is converted by treatment with moist silver chloride into chlorobromide, whilst freshly-precipitated silver oxide converts it into the hydroxide, $C_4H_8N_2SBr(OH)$,[2] a syrup having an alkaline reaction and a bitter taste. Thio-sinamine unites also with a molecule of iodine, and when cyanogen is passed into its alcoholic solution the following reaction takes place:

$$\begin{array}{l} \diagup NH_2 \\ CS \\ \diagdown NH(C_3H_5) \end{array} + \begin{array}{l} CN \\ | \\ CN \end{array} = \begin{array}{l} \diagup NH\text{——}C{=}NH \\ CS \qquad\quad | \\ \diagdown N(C_3H_5)C{=}NH \end{array}$$

The compound thus obtained is deposited in golden-yellow scales, and on heating with dilute sulphuric acid is converted into *oxalylthiosinamine*, the imido-groups being replaced by oxygen. This crystallizes from hot water in lemon-yellow needles, melting at 89°—90°. When warmed with a solution of

[1] Wöhler and Frehrichs, *Ann. Chem. Pharm.* lxv. 335.
[2] Maly, *Zeitsch. Chem.* 1867, 42.

silver nitrate, silver sulphide and allyl-oxyalyl-urea are formed. If however the nitrate be present in excess, silver oxalate and allyl-urea are produced (Maly).

735 *Allyl Cyanamide* or *Sinamine*, $CN.NH(C_3H_5)$, is obtained by heating, on a water-bath, thio-sinamine with freshly-precipitated lead hydroxide. The residue is extracted with alcohol, and this on evaporation leaves a syrup from which, after some months, hard, glistening, monoclinic prisms separate, having the composition $(C_4H_6N_2)_2 + H_2O$. These melt at 100° with loss of water, yielding an imperfectly crystalline mass which quickly absorbs moisture from the air. The syrupy sinamine contains less water than the crystalline hydrate. Sinamine possesses a powerfully-bitter taste, has a strong, alkaline reaction, decomposes ammonia salts, and combines with acids, though it does not form solid salts with the exception of the oxalate. It precipitates many metallic salts and combines with the chlorides of mercury and platinum (Will). According to Hofmann sinamine is probably *triallyl cyanuramide*, $C_3N_3(NH.C_3H_5)_3$.[1]

*Ethyl Allyl Monothiocarbamate*, $CS(NH.C_3H_5)OC_2H_5$, is formed by heating mustard-oil with alcohol. It is an alliaceous-smelling oil boiling at 210°—215°.[2]

*Allyl Dithiocarbamic Acid*, $CS(NH.C_3H_5)SH$. This acid, of which the salts only are known, was termed by Will mustard-oil sulphuretted hydrogen.[3] Its constitution was first determined by Gerhardt.[4] The potassium salt, $C_4H_6NS_2K$, is formed by adding mustard-oil to an alcoholic solution of potassium hydrosulphide until the smell disappears. It is then allowed to evaporate in a vacuum, when it deposits in large rhombic tables. If a solution of potassium sulphide be employed, the salt $CS(NKC_3H_5)SK$ deposits as a white, granular precipitate. Other soluble hydrosulphides and sulphides give similar compounds, and all these salts easily decompose with liberation of oil of mustard.

*Triethyl phosphosinamine*, $SCN(C_3H_5)P(C_2H_5)_3$, is formed by the direct union of mustard-oil with triethyl phosphine. It crystallizes from ether in tables which are isomorphous with thiosinamine. They melt at 68° and decompose at a higher temperature into triethylphosphine sulphide and allyl carbamine.[5]

[1] *Ber. Deutsch. Chem. Ges.* ii. 603.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* ii. 119.
[3] *Ann. Chem. Pharm.* xcii. 59.
[4] *Traité Chim. Org.* ii. 403.
[5] Hofmann, *Ann. Chem. Pharm.* Suppl. i. 57; *Ber. Deutsch. Chem. Ges.* iii. 766.

## THE ACRYL COMPOUNDS.

736 *Acrylaldehyde*, or *Acrolein*, $C_3H_4O$. It has long been known that when the fats are heated a liquid body is formed possessing an intensely pungent and very irritating smell. Buchner endeavoured to isolate it by distilling lard, and he thus obtained a very volatile liquid, and he states that a mouse placed for one minute in air containing some of the vapour of the compound died in fifteen minutes after taking it out.[1] Hess, who prepared this compound from oil of hemp, concluded from certain reactions that it was aldehyde (lampic acid), and states that it is so volatile and attacks the eyes and organs of respiration so violently that any idea of working for a length of time upon the substance must be given up.[2] Brandes, who prepared it from cocoa-nut oil and other fats, could not obtain it in the pure state.[3] He gave some of his product to Berzelius, who ascertained that it is an aldehyde and termed it *acrolein*. Redtenbacher then noticed that this body is not the product of decomposition of the fatty acids but of fats, and is therefore to be regarded as a decomposition product of glycerol, and he pointed out that the production of this pungent substance might serve as the best proof that the fats contain glycerol. He also proved that it is impossible to prepare pure acrolein from the fats, but that it may be readily obtained in the pure state when glycerol is distilled with dehydrating agents such as phosphorus pentoxide, or acid potassium sulphate, and that it is the aldehyde of a monobasic acid to which he gave the name of acrylic acid.[4]

Acrolein is formed from glycerol by the removal of the elements of water:

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array} + 2H_2O.$$

In order to prepare it, one part of anhydrous glycerol is

[1] Gmelin, *Handbook*, ix. 365.
[2] *Ann. Chem. Pharm.* xx. 9.
[3] Gmelin, *loc. cit.*
[4] *Ann. Chem. Pharm.* xlvii. 113.

distilled with two parts of acid potassium sulphate.[1] To obtain it in the anhydrous condition, and to free it from acrylic acid, it is collected in a receiver containing calcium chloride and lead oxide and rectified over calcium chloride.[2] Acrolein is also obtained in large quantity as a by-product in the preparation of œnanthol from castor-oil (Schorlemmer). It may likewise be prepared by the oxidation of allyl alcohol.

Acryl aldehyde is a mobile, powerfully-refracting liquid, boiling at 52°·4, and having a vapour density of 1·897 (Redtenbacher). Its vapour attacks the mucous membranes of the nose and eyes in a frightful manner. Redtenbacher remarks: "In a very highly diluted condition the smell is not altogether unpleasant, being somewhat ethereal, but a few drops of acrolein brought into a room soon bring the company to tears. It chiefly acts upon the eyes, the vapour producing a burning sensation and a copious flow of tears. The eyes remain red, without, however, other evil consequences; but on repeated exposure to the action of acrolein, inflammation sets in, and this lasts for some days. The action cannot however be said to be a poisonous one, inasmuch as even although insensibility may be produced, no further effects are noticed. Its taste is a pungent and burning one." When exposed for some length of time to an atmosphere containing small quantities of the vapour of this body a peculiar feeling is experienced similar to that which is felt after indulgence in moderate quantities of alcohol (Schorlemmer).

737 In the pure state it may be preserved without alteration, but in the impure condition it is soon converted into a white amorphous body which is probably a polymeric modification, and has been termed *disacryl*. Caustic alkalis convert it into a resin, and alcoholic potash or sodium ethylate transforms it into monobasic amorphous *hexacrolic acid*, $C_{18}H_{24}O_6$, whose salts are amorphous.[3] Acrolein absorbs hydrochloric acid, a crystalline compound being formed to which Geuther and Cartmell gave the name of *acrolein hydrochloride*, $C_3H_5ClO$.[4] On oxidation it is converted into $\beta$-chlorpropionic acid, and it is therefore the aldehyde of this substance.[5] It forms white silky needles, which

[1] Geuther and Cartmell, *ib.* cxii. 1; Geuther and Hübner, *ib.* cxiv. 35; Claus, *Zeitsch. Chem.* iv. 156.
[2] Aronstein, *Ann. Chem. Pharm.* Suppl. iii. 180.
[3] Claus, *Ann. Chem. Pharm.* Suppl. ii. 117; Alsberg, *Zeitsch. Chem.* i. 39.
[4] *Ann. Chem. Pharm.* cxii. 3.
[5] Krestownikow, *Ber. Deutsch. Chem. Ges.* x. 1104.

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have a faint rancid smell, are insoluble in water, but dissolve in alcohol. On heating with caustic potash it yields a polymeride of acrolein termed *metacrolein*. This is slightly soluble in hot water, but dissolves in alcohol, and crystallizes in long needles which melt at 50° and have a peculiar aromatic smell and a cooling and afterwards burning taste. On distillation it decomposes with partial re-formation of acrolein, and it is also converted into this substance by heating with aqueous hydrochloric acid, whilst it unites the gaseous acid forming chlorpropionaldehyde. Phosphorus pentachloride acting on the latter compound yields $\beta$-chlorpropidene chloride, $CH_2Cl.CH_2.CHCl_2$, a liquid boiling at 146°—148°. It can also be obtained in a similar way, together with other products, from acrolein.[1] When, however, hydrochloric acid acts on an alcoholic solution of acrolein, diethyl chlorhydrin is formed,[2] and when heated with alcohol and acetic acid, propenylethyl ether is produced (Alsberg):

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array} + 3HO.C_2H_5 = \begin{array}{l} CH_2.OC_2H_5 \\ | \\ CH.OC_2H_5 \\ | \\ CH_2.OC_2H_5 \end{array} + H_2O.$$

Some doubt has, however, been lately thrown upon the last statement.[3]

Acrolein is reduced in presence of zinc and hydrochloric acid to allyl alcohol and *acropinacone*, $CH_2{=}CH(OH).CH(OH).CH{=}CH_2$; this latter body is a camphor-like liquid boiling at 160°—180° (Linnemann). Acrolein absorbs oxygen on exposure to air and is converted into acrylic acid, a body which is also obtained by the action of silver oxide or an ammoniacal silver solution, with deposition of a silver mirror, though it is not obtained when more violent oxidizing agents are employed, such as dilute nitric acid, which yields glycollic acid and oxalic acid.[4]

If ammonia gas be led into an ethereal solution of acrolein,[5] or if acrolein be dissolved in concentrated ammonia,[6] an amorphous body termed *acrolein ammonia* is formed, which has the formula $2(C_6H_9NO) + H_2O$. This is insoluble in cold alcohol and ether, and combines with acids to form amorphous salts.

[1] Van Romburgh, *Bull. Soc. Chim.* xxxvi. 459; xxxvii. 98.
[2] Alsberg, *Jahresb.* 1864, 495.
[3] Tawildarow, *Ber. Deutsch. Chem. Ges.* xii. 1487.
[4] Claus, *Ann. Chem. Pharm.* Suppl. ii. 118.
[5] Redtenbacher; Hübner and Geuther.
[6] Claus, *Ann. Chem. Pharm.* cxxx. 185.

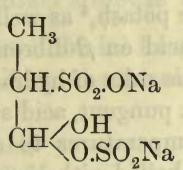
It therefore probably belongs to the family of the aldines (p. 75). It decomposes on distillation, and amongst the products *picoline*, $C_6H_7N$, is found,[1] a body occurring in animal oils.

## Allidene Compounds.

738 Like other aldehydes acrolein acts in certain respects as the oxide of a dyad radical termed *allidene*, $C_3H_4$. The following compounds are known belonging to the series. They are obtained in a similar way to the ethidene compounds[2] (see p. 67).

| | | B.P. |
|---|---|---|
| Allidene diethyl ether, or Acrolein acetal, | $C_3H_4\{^{OC_2H_5}_{OC_2H_5}$ | 140°—145° |
| Allidene dichloride, | $C_3H_4\{^{Cl}_{Cl}$ | 85° |
| Allidene chlorethylate, | $C_3H_4\{^{Cl}_{OC_2H_5}$ | 115°—120° |
| Allidene diacetate, | $C_3H_4\{^{OC_2H_3O}_{OC_2H_3O}$ | 180° |

*Sodium Sulphallidene-Sulphite*, or *Sulphacrolein Potassium Sulphite*, $C_3H_5(OH)(SO_3Na)_2$. This compound is obtained by adding acrolein to a concentrated solution of acid sodium sulphite until its smell disappears. The compound has the following constitution:



Alcohol precipitates it as a gummy mass, solidifying to a wart-like solid. Acids liberate from it sulphur dioxide but no acrolein, and an ammoniacal solution of barium chloride precipitates barium sulphite, whilst the solution contains the sodium salt of *α-sulphopropionaldehyde*, $CH_3.CH(SO_3H).CHO$. On oxidation with silver oxide it is converted into *α*-sulphopropionic acid, a body which is also obtained by the action of fuming sulphuric acid on propionitril. Sodium amalgam added to its solution forms *oxypropane-sulphonic acid*, $CH_3CH(SO_3H).CH_2.OH$. This

[1] Baeyer, *ib.* clv. 283.
[2] Hübner and Geuther; Aronsheim; van Romburgh.

is also obtained by the action of sulphur trioxide on propyl alcohol, and its potassium salt is easily produced by heating allyl alcohol with a concentrated solution of acid potassium sulphite. It forms white, pearly needles.[1]

## Acrylic Acid, $C_3H_4O_2$.

739 This acid was obtained by Redtenbacher by heating impure acrolein with silver oxide, purifying the silver salt thus obtained, and then decomposing this with sulphuretted hydrogen. According to Claus the best method of preparation is to place the freshly precipitated oxide in a flask provided with inverted condenser, and gradually to add a solution of 1 part of acrolein in 3 parts of water, the operation being conducted in the dark. After the reaction is complete the whole is warmed to the boiling point, and sodium carbonate added to alkaline reaction, the filtrate evaporated, and the residue distilled with sulphuric acid. To prepare the anhydrous acid, the pure lead salt is mixed with sand and decomposed at 170° in a current of sulphuretted hydrogen.[2]

Acrylic acid is also easily obtained by intimately mixing $\beta$-iodopropionic acid with the equivalent quantity of lead oxide, covering the mixture with lead oxide and distilling.[3] It is likewise produced when $\beta$-iodopropionic acid is treated with an alcoholic solution of caustic potash,[4] as well as by the action of zinc and dilute sulphuric acid on $\beta$-dibrompropionic acid,[5] and also by the distillation of the salts of hydracrylic acid.[6]

It is a liquid possessing a pungent, acid smell, boiling at 140°, and solidifying at low temperatures to crystals which melt between 7° and 8°.[7] When boiled with zinc and dilute sulphuric acid, or treated with water and sodium amalgam, it is converted into propionic acid.[8] Fused with caustic potash it yields acetic and formic acids:[9]

$$CH_2{=}CH.CO_2K + KOH + H_2O{=}CHO.OK + CH_3.CO_2K + H_2.$$

[1] M. Müller, *Ber. Deutsch. Chem. Ges.* vi. 1441.
[2] *Ann. Chem. Pharm.* Suppl. ii. 123.
[3] Wislicenus, *ib.* clxvi. 2.
[4] Erlenmeyer and Schneider, *Ber. Deutsch. Chem. Ges.* iii. 339.
[5] Caspary and Tollens, *Ann. Chem. Pharm.* clxvii. 241.
[6] Beilstein, *ib.* cxxii. 372.
[7] Linnemann, *Ann. Chem. Pharm.* clxxi. 294.
[8] *Ib.* cxxv. 317.
[9] Erlenmeyer, *ib.* cxci. 376.

It combines with bromine to form β-dibrompropionic acid, with hydriodic acid to form β-iodopropionic acid,[1] and with hypochlorous acid to form chlorolactic acid.[2] When hydrochloric acid is led into its alcoholic solution the ethyl salt of β-chlorpropionic acid is formed.[3]

*Potassium acrylate*, $C_3H_3O_2K$, forms deliquescent needles. *Sodium acrylate*, $C_3H_3O_2Na$, crystallizes in microscopic needles, difficultly soluble in absolute alcohol but easily soluble in strong spirit.[4] *Calcium acrylate*, $(C_3H_3O_2)_2Ca$, forms thick needles which easily lose acid. *Zinc acrylate*, $(C_3H_3O_2)_2Zn$, crystallizes in glistening scales. *Lead acrylate*, $(C_3H_3O_2)_2Pb$, is a very characteristic salt, and crystallizes from water in glistening needles soluble in alcohol. *Silver acrylate*, $C_3H_3O_2Ag$, is a curdy precipitate, and crystallizes from hot water in needles or prisms.

*Ethereal Salts of Acrylic Acid.* Of these the following have been prepared by Caspary and Tollens,[5] by acting with zinc and sulphuric acid upon the corresponding compounds of β-dibrompropionic acid:

| | B.P. |
|---|---|
| Methyl acrylate, | 80°—85° |
| Ethyl acrylate, | 101°—102° |
| Allyl acrylate, | 119°—124° |

## Substitution-Products of Acrylic Acid.

740 These have been obtained from the dichlor- and dibrompropionic acids and from the trisubstituted lactic acids

| | | M.P. | B.P. |
|---|---|---|---|
| [6] α-Chloracrylic acid, $CH_2{=}CCl.CO_2H$ | Liquid. | — | 176°-181° |
| [7] β-Chloracrylic acid, $CHCl{=}CH.CO_2H$ | Plates. | 84°-85° | — |
| [8] α-Dichloracrylic acid, $C_3H_2Cl_2O_2$ | Rhombic prisms. | 85°-86° | — |

[1] Wislicenus, *ib.* clxvi. 1.
[2] Melikow, *Ber. Deutsch. Chem. Ges.* xii 2227.
[3] Linnemann, *Ann. Chem. Pharm.* clxiii. 96.
[4] V. Zotta, *Ann. Chem. Pharm.* cxcii. 105
[5] *Ann. Chem. Pharm.* clxvii. 241.
[6] Beckurts and Otto, *Ber. Deutsch. Chem. Ges.* x. 1948.
[7] Pinner, *Ann. Chem. Pharm.* clxxix. 85; Wallach, *ib.* cxciii. 28; cciii. 94, Werigo and Melikow, *Ber. Deutsch. Chem. Ges.* x. 1499.
[8] Bennet and Hill, *Ber. Deutsch. Chem. Ges.* xii. 656.

| | | M.P. | B.P. |
|---|---|---|---|
| [1] β-Dichloracrylic acid, $C_3H_2Cl_2O_2$ | Monoclinic prisms. | 76°-77° | — |
| [2] α-Bromacrylic acid, $CH_2{=}CBr.CO_2H$ | Rectangular tables. | 69°-71° | — |
| [3] β-Bromacrylic acid, $CHBr{=}CH.CO_2H$ | Needles. | 115°-116° | — |
| [4] Dibromacrylic acid, $C_3H_2Br_2O_2$ | Rhombic prisms. | 85-86° | 243-250° |

β-Bromacrylic acid and its ethyl salt easily undergo conversion into amorphous bodies possessing the formula $(C_3H_4O_3)_n$, and termed *acryl colloids*. They are insoluble in water, but swell up with this liquid to form a gelatinous mass.

## CROTYL COMPOUNDS.

741 *Crotyl Alcohol*, $CH_3CH{=}CH.CH_2OH$, is formed together with butyraldehyde and normal butyl alcohol when crotonaldehyde (p. 403) or butyl chloral (p. 166) is treated with iron filings and acetic acid. It is also obtained together with carbon dioxide and formic acid by heating butenyl alcohol (p. 377) with oxalic acid. It is a pungent-smelling liquid boiling at 118° to 120°, and is converted by hydriodic acid into secondary butyl iodide.

*Crotyl Iodide*, $C_4H_7I$, is obtained by acting with iodine and phosphorus upon butenyl alcohol. It boils at 131°—133°, smells like allyl iodide, and like this body forms a crystalline compound with mercury.[5]

*Isocrotyl Mustard Oil*, $(CH_3)_2C{=}CH.N.CS$. When isobutylene dibromide is heated with ammonia, *isocrotylamine*, $(CH_3)_2C{=}CH.NH_2$, a body boiling at 75°—78° is formed, together with isobutylene diamine, and the former body is converted into *isocrotyl thiocarbimide* by treatment with carbon disulphide and distillation of the product with corrosive sublimate. This body is a liquid smelling like mustard oil, boiling at 179°, and yielding when treated with ammonia a thio-urea resembling thio-sinamine (p. 394) but melting at 85°.[6]

[1] Wallach, *loc. cit.*
[2] Wagner and Tollens, *Ann. Chem. Pharm.* clxxi. 340; Wallach, *loc. cit.*
[3] Wallach, *ib.*
[4] Jackson and Hill, *Ber. Deutsch. Chem. Ges.* xi. 1673; Hill, *ib.* xii. 660; Petri, *Ann. Chem. Pharm.* cxcv. 70.
[5] Lieben and Zeisel, *Monatsh. Chem.* i. 318, 840.
[6] Hofmann, *Ber. Deutsch. Chem. Ges.* vii. 516; xii. 992.

## The Crotonic Acids, $C_4H_6O_2$.

**742** In 1858 Schlieppe gave the name of crotonic acid to an oily liquid which he obtained from croton oil (*Croton tiglium*).[1] Other chemists, however, were not able to obtain this again.[2] It probably does not always occur in the oil, and perhaps is identical with the $\beta$-crotonic acid, mentioned below. The name crotonic acid was, however, retained to designate the solid acid which was obtained from the nitril and aldehyde, now to be described.

*a-Crotonaldehyde*, $C_4H_6O$. By heating acetaldehyde with certain saline solutions, Lieben obtained a liquid possessing the above composition, to which he gave the name of *aldehyde-ether*;[3] whilst Bauer found that a very pungent smelling liquid is obtained by the action of zinc chloride on aldehyde, and he considered this to be a polymeric modification, and termed it *acraldehyde*.[4] Kekulé then showed that these two bodies are identical, and that they are crotonaldehyde,[5] giving the following equation for its formation:

$$\begin{matrix} CHO.CH_3 \\ \\ CH_3.CHO \end{matrix} \qquad \begin{matrix} CH.CH_3 \\ \| \\ CH.CHO \end{matrix} + H_2O.$$

It is probable that aldol (p. 168) is first formed, and that this then decomposes into water and crotonaldehyde. The latter compound is also formed when acetylene, $C_2H_2$, is dissolved in concentrated sulphuric acid, and the liquid distilled with water.[6] Berthelot considered the body thus obtained to be vinyl alcohol, $C_2H_3.OH$. Instead of acetylene, bromethylene may also be employed.[7] Crotonaldehyde also occurs in the products of distillation of crude spirit.[8] In order to prepare it, pure aldehyde is heated with a small quantity of zinc chloride and a few drops of water for one or two days to 100°. The unaltered acetaldehyde is distilled off and the crotonaldehyde obtained from the residue by distillation with water (Kekulé). It is also easily obtained when ten volumes

[1] *Ann. Chem. Pharm.* cv. 24.
[2] Geuther, *Zeitsch. Chem.* 1870, 26; Geuther and Fröhlich, *ib.* 549.
[3] *Ann. Chem. Pharm.* Suppl. i. 117.
[4] *Ib.* cxvii. 142.
[5] *Ib.* clxii. 92, 309.
[6] Lagermark and Eltekow, *Ber. Deutsch. Chem. Ges.* x. 637; xii. 693.
[7] Zeisel, *Liebeg's Ann.* cxci. 369.
[8] Krämer and Pinner, *Ber. Deutsch. Chem. Ges.* iii. 75.

of acetaldehyde are heated for twenty-four hours to 100° with one volume of concentrated solution of sodium acetate and the product fractionated.[1] It may also be readily prepared by distilling aldol under the ordinary atmospheric pressure.[2]

Crotonaldehyde is a mobile liquid possessing at first a fruit-like, but afterwards a very pungent smell. It boils at 104°—105°, and at 0° has a specific gravity of 1·033. It combines with hydrochloric acid to form β-chlorbutyraldehyde. On exposure to air or in contact with silver oxide it yields α-crotonic acid.

*Crotonitril*, $C_4H_5N$, is formed by the action of water on mustard-oil, and it is often contained in this substance in large quantity. It is also easily formed by heating allyl iodide with potassium cyanide.[3] If, however, allyl chloride be brought in contact with potassium cyanide and alcohol, the nitril of β-ethoxybutyric acid is formed, a liquid boiling at 173°—174°.[4]

Crotonitril is an unpleasantly alliaceous-smelling liquid, boiling at 119°, and at 0° having a specific gravity of 0·8491. It is converted by hydrochloric acid into β-chlorbutyric acid (Pinner).

743 *α-Crotonic Acid*, $CH_3.CH{=}CH.CO_2H$. This compound, which is also termed solid crotonic acid, was obtained by Will and Körner by heating its nitril with alcoholic potash.[5] It likewise is formed by distilling β-oxybutyric acid,[6] or by heating alcoholic potash with β-chlorbutyric [7] or with the ethyl salt of α-brombutyric acid.[8] It is also a constituent of crude pyroligneous acid.[9] It dissolves in 12 parts of cold water, more easily in boiling water, and crystallizes from this on cooling in fine woolly needles, whilst on slow evaporation, its solution deposits large monoclinic prisms, melting at 72°, and easily subliming in tablets. Its smell resembles that of butyric acid, and it boils at 189°. When treated with sodium amalgam and water it remains unaltered, but, on the other hand, it combines with hydrobromic and hydriodic acids to form substituted butyric

[1] Lieben and Zeisel, *Monatsh. Chem.* i. 820.
[2] Newburg, *Comptes Rendus*, xcii. 196.
[3] Claus, *Ann. Chem. Pharm.* cxxxi. 58; Rinne and Tollens, *ib.* clix. 105.
[4] Rinne, *Ber. Deutsch. Chem. Ges.* vi. 389; Pinner, *ib.* xii. 2053.
[5] *Ann. Chem. Pharm.* cxxv. 272; Claus, *ib.* cxxxi. 58.
[6] Wislicenus, *Zeitsch. Chem.* 1869, 325.
[7] Balbiano, *Ber. Deutsch. Chem. Ges.* xi. 348.
[8] Hell and Lauber, *ib.* vii 560.
[9] Krâmer, *Ber. Deutsch. Chem. Ges.* xi. 1356.

acids, which are converted in presence of nascent hydrogen into normal butyric acid.[1] On oxidation with chromic acid, it yields acetaldehyde and acetic acid. This decomposition, as well as its formation from aldehyde, leave no doubt concerning its constitution. On the other hand, we should expect, from its synthesis from allyl iodide, that its formula would be $CH_2{=}CH.CH_2.CO_2H$. Only one acid of this constitution is known, namely *β*-crotonic acid, which will be described further on. This is easily converted on heating into the *a*-compound, and the same is probably also the case with the nitril, which is doubtless first formed from mustard-oil or allyl iodide, and in favour of this view is the fact that crotonitril yields acetic acid on oxidation, whilst this acid is not obtained in the same way from the allyl compounds.[2] Its constitution, therefore, must be $CH_3.CH{=}CH.CN$. On the other hand, Pinner gives to it the following constitution, $CH_2{=}CH.CH_2.CN$, and assumes that by the action of hydrochloric acid or caustic potash, *β*-crotonic acid is first formed, and that this, by the action of hydrochloric acid or water, combines to form *β*-chlorpropionic acid, $CH_3.CHCl.CH_2.CO_2H$, or *β*-oxybutyric acid, $CH_3.CH(OH).CH_2.CO_2H$, which then decompose further with formation of *a*-chlorcrotonic acid.

*a-Chlorcrotonic Acid*, $CH_3.CH{=}CCl.CO_2H$, is formed when trichlorbutyric acid is treated with zinc and hydrochloric acid,[3] or with zinc-dust and water,[4] or when butyl chloral (p. 166) is boiled with a solution of yellow prussiate of potash.[5] It crystallizes in long needles, melting at 12°·5, and dissolves in 49·8 parts of water; the solution producing blisters when brought on to the skin. The acid melts at 97°·5,[6] boils at 212°, and combines with nascent hydrogen to form *a*-crotonic acid.

744 *β-Crotonic Acid*, $CH_2{=}CH.CH_2.CO_2H$. This compound, which was first described by Geuther, is sometimes termed liquid crotonic acid or isocrotonic acid; it was obtained by him from acetacetic ether.[7] If this be treated with an excess of phosphorus pentachloride, the chlorides of two crotonic acids are formed. If these be decomposed by water and distilled, the

[1] Hemilian, *Ann. Chem. Pharm.* clxxiv. 324; Alberti, *Ber. Deutsch. Chem. Ges.* ix. 1195.
[2] Kekulé and Rinne, *Ber. Deutsch. Chem. Ges.* vi. 386.
[3] Krâmer and Pinner, *Ann. Chem. Pharm.* clviii. 37.
[4] Sarnow, *Ann. Chem. Pharm.* clxiv. 93.
[5] Wallach, *Ber. Deutsch. Chem. Ges.* x. 1530.
[6] Kahlbaum, *ib.* xii. 2338.
[7] Fröhlich and Geuther, *Zeitsch. Chem.* 1869, 270; Geuther, *ib.* 1871, 242.

first distillate contains *chlorisocrotonic acid*, $CH_2{=}CCl.CH_2.CO_2H$, and the second, *β-chlorcrotonic acid*, or *chlortetracrylic acid*, $CH_3.CCl{=}CH.CO_2H$, crystallizing in monoclinic prisms or needles, melting at 94°—94°·5, and at 12°·5 dissolving in 44·4 parts of water (Kahlbaum). It boils at 206°—211°, and is converted by sodium amalgam and water into *α*-crotonic acid. The chlorisocrotonic acid melts at 59°·5 and crystallizes from water in four-sided prisms having oblique terminal faces. It boils at 194°·8, but volatilizes easily at the ordinary temperature, and it dissolves at 7° in 79 parts of water. It is converted by sodium amalgam and water into isocrotonic acid, a liquid having a pungent smell resembling butyric acid. This is miscible in every proportion with water, does not solidify at −15°, and boils at 171°·9, a large portion of it passing into solid crotonic acid. This change takes place more completely when it is heated to 180° in a closed tube.[1] This same substance is also formed when isocrotonic acid combines with hydrobromic acid, and the brombutyric acid thus formed is decomposed by alkalis. The latter acid, but not isocrotonic acid, combines with nascent hydrogen to form butyric acid. Isocrotonic acid occurs also in crude pyroligneous acid (Krämer and Grodski).

745 *Methacrylic acid*, $\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!C.CO_2H$. The ethyl salt of this acid was obtained by Frankland and Duppa by heating ethyl oxyisobutyrate with phosphorus trichloride. It is a mobile liquid which has an unpleasant smell of mouldy fungus. It is easily decomposed by alcoholic potash, and from the potassium salt thus obtained methacrylic acid is readily got by distillation with sulphuric acid.[2] This same compound is also formed, together with large quantities of oxyisobutyric acid, when bromisobutyric acid is heated with 20 parts of water.[3] It is best, however, prepared by boiling citrabrompyrotartaric acid, $C_3H_5Br(CO_2H)_2$, a body to be described under citric acid, with carbonate of soda solution.[4] It is found also in small quantity as an ethereal salt in Roman cumin oil.[5] It is tolerably soluble in water and crystallizes in long prisms which melt at 16° and boil at 160°·5. It combines with nascent hydrogen to form isobutyric acid, and

[1] Hemilian, *Ann. Chem. Pharm.* clxxiv. 322.
[2] *Journ. Chem. Soc.* xviii. 139.
[3] Thomsen, *Ann. Chem. Pharm.* cc. 86.
[4] Fittig and Landolt, *ib.* clxxxviii. 81.
[5] Kopp, *ib.* cxcv. 82.

on fusion with caustic potash decomposes into formic and propionic acids. When heated to 130° it is converted into a polymeric modification, which is also formed when the acid is allowed to remain in contact with hydrochloric acid, and gradually when it is kept in a closed vessel. This is a porcelain-like mass, which is insoluble in all indifferent solvents. It gelatinizes in water, forming a transparent thick liquid from which a white stringy mass separates out on heating. It dissolves slowly in ammonia, and from this solution calcium chloride or barium chloride precipitates an elastic gummy mass, which on heating with water becomes hard, but on cooling again assumes an elastic condition. It is scarcely attacked by fuming nitric acid, concentrated sulphuric acid, or by caustic potash, and is decomposed above 300° without forming methacrylic acid.[1]

## ACIDS HAVING THE COMPOSITION, $C_5H_8O_2$.

### Angelic Acid, $C_5H_8O_2$,

746 This acid was discovered by Buchner in the roots of *Angelica archangelica*,[2] and investigated more completely by Meyer and Zeuner, who found that the roots also contain valeric acid.[3] Angelic acid is also found in large quantities in the sumbul- or moschus- root[4] (*Eurangium sumbul*), a plant growing largely in Turkistan and on the Amur, and the roots of which have been long used as an excitant. Gerhardt found that angelic acid can be easily obtained when the Roman oil of cumin (*Anthemis nobilis*) is treated with alcoholic potash, and he believed that the oil contained the aldehyde of angelic acid, which, however, he did not succeed in isolating.[5] Demarçay, in another investigation of this oil, came to quite other conclusions. According to him, it is essentially a mixture of valeric acid and the angelic salts of butyl and amyl.[6] That it does contain ethereal salts has been shown also by Köbig; no valerate is, however, contained in it,

[1] Engelhorn, *Liebig's Ann.* cc. 70. [2] *Ann. Chem. Pharm* xlii. 226.
[3] *Ann. Chem. Pharm.* lv. 317.
[4] Reinsch, *Jahrb. pr. Pharm.* vii. 79; Reinsch and Hopf, *ib.* xi. 217; Reinsch and Ricker, *ib.* xvi. 12.
[5] *Ann. Chem. Pharm.* lxvi. 235. [6] *Compt. Rend.* lxxvii. 360.

but an ethereal salt of an acid, tiglic acid, isomeric with angelic acid.[1] By fractional distillation he obtained the following:

| | | B.P. |
|---|---|---|
| Isobutyl isobutyrate, | $C_4H_7O_2(C_4H_9)$ | 147°—148° |
| Isobutyl angelate, | $C_5H_7O_2(C_4H_9)$ | 177°—177°·5 |
| Amyl angelate, | $C_5H_7O_2(C_5H_{11})$ | 200°—201° |
| Amyl tiglate, | $C_5H_7O_2(C_5H_{11})$ | 204°—205° |

Of these the isobutyrate is contained only in small quantity. In addition to these the oil contains tiglates and angelates of an hexyl alcohol, which cannot be distilled without decomposition, and of anthemol, $C_{10}H_{15}(OH)$.

In order to prepare angelic acid, 100 grams of Roman oil of cumin is distilled in a water-bath with a reversed condenser with 200 grams of ordinary alcohol and 56 grams of caustic potash for eight to ten hours. The liquid is then distilled off, water added to the residue, and the whole again distilled, in order to remove hydrocarbons, the liquid acidified with sulphuric acid, and the distillation again continued until no further acid comes over. The oil which swims upon the top is removed, and the acid distillates which follow neutralized with carbonate of soda, the solution evaporated, and the residue decomposed with sulphuric acid, when again an oil separates out which is united with the first portion. By fractional distillation the acid may be partly separated,[2] but a quicker method is to collect the fractions boiling between 181° and 195° and convert these into the calcium salt. The cold saturated solution on warming to 60°—70° deposits calcium angelate, which may be purified by a repetition of this process.[3]

Angelic acid is difficultly soluble in cold, but readily soluble in hot water, and crystallizes in long monoclinic prisms, which have an aromatic smell and melt at 44°—44°·5. It boils at 185°, and when boiled for some time, as well as when heated with sulphuric acid to 100°, is converted into tiglic acid. On fusion with caustic potash it decomposes into acetic and propionic acids, and it combines with bromine and hydrobromic acid to form brominated valeric acids. Sodium amalgam and water do not alter it, but when heated with hydriodic acid and red phosphorus to 180°—200° it is converted into a valeric acid,[4]

[1] *Liebig's Ann.* cxcv. 92.
[2] Kopp, *Liebig's Ann.* cxcv. 81.
[3] Pagenstecher, *Liebig's Ann.* cxcv. 108.
[4] Ascher, *Ber. Deutsch. Chem. Ges.* ii. 685.

which according to Schmidt is methyl-ethyl-acetic acid. If the dibrom-valeric acid be heated with sodium amalgam and water the bromine is removed, but instead of angelic acid its isomeride tiglic acid is formed. The change from angelic to tiglic acid also takes place slowly, simply on keeping the first-named acid.[1]

*Calcium Angelate*, $(C_5H_7O_2)_2Ca + 2H_2O$, dissolves, as has been stated, more readily in cold than in hot water, and the solution saturated at 17°·5 contains 23 parts of the anhydrous salt; but when heated to 35°—40°, splendid glistening long needle-shaped crystals separate out, the quantity increasing with the rise of temperature, so that at 60°—70° a thick crystalline semi-solid mass is formed, and if the experiment be carried out in a closed tube the whole dissolves again completely on cooling (Kopp).

## 747 Tiglic Acid, $C_5H_8O_2$,

was first prepared by Frankland and Duppa by the action of phosphorus trichloride upon ethyl metho-ethoxalate.[2] It was termed by them *methyl-crotonic acid*. Geuther and Fröhlich[3] obtained an acid of this composition from croton oil (*Croton tiglium*), which contained, together with the glyceride of this acid, those of other volatile and non-volatile acids. This acid they considered to be identical with methyl-crotonic acid, and the correctness of this supposition was proved by Schmidt and Berendes.[4] It is also obtained by the distillation of *α*-methyl-*β*-oxybutyric acid, $CH_3.CH(OH).CH(CH_3).CO_2H$[5] or when this acid is heated with concentrated hydriodic acid.[6] It is, however, best prepared, together with angelic acid, from Roman cumin-oil. Tiglic acid dissolves with some difficulty in cold, but readily in hot water, and crystallizes in triclinic tables or prisms, which melt at 64°·5, whilst a mixture of this acid with somewhat more than a molecular proportion of angelic acid is liquid at the ordinary temperature. It possesses an aromatic smell resembling that of benzoic acid, and boils at 198°·5, yielding a vapour which causes violent coughing. When heated with iodine and phosphorus to 160° it is transformed into methyl-ethyl-acetic acid, whilst treated with bromine and hydrobromic

[1] Schmidt, *Ann. Chem. Pharm.* ccviii. 249
[2] *Ann. Chem. Pharm.* cxxxvi. 9.
[3] *Zeitsch. Chem.* 1870, 459.
[4] *Ann. Chem. Pharm.* cxci. 94.
[5] Rohrbeck, *ib.* clxxxviii. 235.
[6] Rücker, *ib.* cci. 61.

acid it yields the same products as does angelic acid, and like this latter acid it yields acetic and propionic acids on fusing with caustic potash.

*Calcium Tiglate*, $(C_5H_7O_2)_2Ca + 3H_2O$, is more difficultly soluble in cold water than calcium angelate, 100 parts of the solution saturated at 17° containing 6·05 parts of the anhydrous salt. It is much more soluble in hot water, and crystallizes on cooling in white plates (Kopp).

The several reactions by which tiglic acid is formed leave no doubt as to its constitution, but that of angelic acid has not yet been definitely fixed. That angelic acid yields the same reactions as tiglic acid does with bromine, hydrobromic acid, hydriodic acid, &c., is explained by the fact that it is readily converted into this latter acid. It, therefore, seems probable that the two acids stand to one another in the same relation as the two crotonic acids do. The following formulæ would then represent their constitution:

Angelic Acid. $CH_2{=}C(CH_3)CH_2.CO_2H$.

Tiglic Acid. $CH_3.CH{=}C(CH_3)CO_2H$.

748 *Tiglicaldehyde*, $C_5H_8O$. Deville, in 1843, found amongst the products of the dry distillation of guiacum resin, a liquid of the above composition to which he gave the name of *guajacen*, adding that when exposed to the air this liquid absorbed oxygen, being converted into a body crystallizing in fine plates.[1] This body, which was afterwards known as *guajol*, was considered by Gerhardt[2] to be angelicaldehyde, but Hlasiwetz and v. Gilm[3] disproved this supposition, since on fusing with caustic potash it yielded no angelic acid. That guajol is the aldehyde of tiglic acid was then recognized by Herzing, who showed that the crystals produced by the absorption of oxygen when the liquid is exposed to the atmosphere, are those of tiglic acid.[4]

Tiglicaldehyde has also been prepared by Lieben and Zeisel by the condensation of a mixture of acetaldehyde and propionhyde.[5] It is a liquid boiling at about 118°, having a sweet, burning taste and a narcotic smell resembling that of bitter almonds.

*Allyl-acetic Acid*, $CH_2{=}CH.CH_2.CH_2.CO_2H$. The ethyl salt of this acid is obtained when allyl acetacetate is heated with dry sodium ethylate to 150°—160°.[6] The acid prepared

[1] *Compt. Rend.* xvii. 1143; xix. 134.
[2] *ib.* xxvi. 226.
[3] *Ann. Chem. Pharm.* vi. 379.
[4] *Monatsch. Chem.* iii. 118.
[5] *Ber. Deutsch. Chem. Ges.* xiv. 932.
[6] Zeidler, *Ann. Chem. Pharm.* clxxxvii. 39.

from this is an oily liquid boiling at 187°—189°,[1] possessing an odour resembling that of valeric acid. It is also formed by heating allyl-malonic acid.[2] Dilute nitric acid oxidizes it to succinic acid. Its calcium salt, $(C_5H_7O_2)_2Ca + 2H_2O$, forms pearly glistening plates which dissolve readily in water.

*Dimethyl-acrylic Acid*, $(CH_3)_2C{=}CH.CO_2H$, was first obtained by Semljanizin and Saytzew by the action of phosphorus trichloride on $\beta$-oxyvaleric acid, and supposed to be angelic acid.[3] Miller then obtained it by distilling the oxyacid with dilute sulphuric acid.[4] It is readily soluble in water and forms monoclinic prisms which melt at 69°·5—70°.

## ALCOHOLS HAVING THE FORMULA $C_6H_{12}O$.

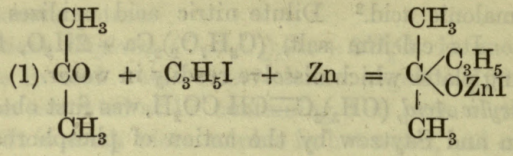
Only secondary and tertiary alcohols of this group are known.

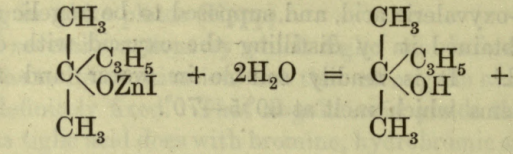
749 *Methyl-isocrotyl Carbinol* or *Butallyl-methyl Carbinol*, $CH_2{=}CH.CH_2.CH_2.CH(OH).CH_3$. By the action of allyl iodide on ethysodacetacetate, *ethyl-allyl-acetacetate*, $CH_3.CO.CH(C_3H_5)CO_2.C_2H_5$, is obtained, a liquid boiling at 206° and yielding a beautiful crimson-red colour with ferric chloride. Alcoholic potash decomposes this with formation of allyl-acetic acid (p. 410), and *allyl-acetone* or *methyl-isocrotyl ketone*, $CH_2{=}CH.CH_2.CH_2.CO.CH_3$, which boils at 128°—130°, and has a characteristic unpleasant smell.[5] When this is mixed with water and ether, and sodium gradually added, the secondary alcohol is formed; this boils at 138°—139°, has at 16° a specific gravity of 0·842, and possesses a characteristic sweet smell somewhat resembling that of allyl alcohol. On heating with acetic anhydride the acetate is formed, boiling at 147°—149°.[6] The compound described as diallyl hydrate, whose formation is referred to under diallyl, is doubtless identical with the secondary alcohol.

*Dimethyl-allyl Carbinol*, $C_3H_5.C(CH_3)_2OH$. To prepare this compound, a mixture of equal molecules of acetone and allyl

[1] Messerschmidt, *ib.* ccviii. 92.
[2] Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 170.
[3] *Lieb. Ann.* excvii. 73.
[4] *Ib.* cc. 261.
[5] Zeidler, *Lieb. Ann.* clxxxvii. 30.
[6] J. K. Crow, *Lieb. Ann.* cci. 42.

iodide is brought very slowly into contact with zinc cooled with ice, and the product distilled with water:





Dimethyl-allyl carbinol is a liquid possessing a faint, pleasant, camphor-like smell. It boils at 119°·5, has at 0° a specific gravity of 0·8438, and combines with water to form the hydrate, $C_6H_{12}O + H_2O$, boiling at 116°—117°.[1] On oxidation with chromic acid solution it first forms *β*-oxyvaleric acid, formic acid, and acetone, whilst potassium permanganate yields a larger proportion of *β*-oxyvaleric acid, together with formic and oxalic acids.[2]

When the alcohol is heated with acetic anhydride to 150° the acetate is formed. This is a liquid possessing a fruit-like smell, boiling at 137°·5, and having at 0° a specific gravity of 0·9007.

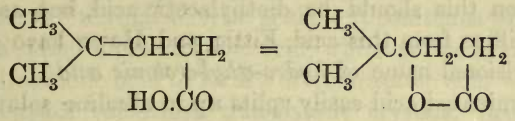
*Dimethyl-isoallyl Carbinol*, $CH_3.CH{=}CH.C(CH_3)_2OH$, is obtained by the action of *α*-crotonyl chloride on zinc-methyl, and is a thick oily liquid which boils between 110° and 115°.[3]

## ACIDS HAVING THE COMPOSITION, $C_6H_{10}O_2$.

750 *Pyroterebic Acid*, or *Isopropyl-acrylic Acid*, $(CH_3)_2C{=}CH.CH_2.CO_2H$. Terebic acid, $C_7H_{10}O_4$, which is formed by the oxidation of oil of turpentine with nitric acid, is converted on heating, as was found by Babourdin, into carbon dioxide and a new compound which he termed *acide pyroterebilique*.[4] This last acid was further examined by several chemists,[5] who, finding that

[1] M. and A. Saytzew, *Ann. Chem. Pharm.* clxxxv. 151, 175.
[2] Schirokow, *Journ. Prakt. Chem.* [2], xxiii. 205.
[3] Pawlowsky, *Ber. Deutsch. Chem. Ges.* v. 331.
[4] *N. Journ. Pharm.* vi. 196.
[5] Chautard, *Ann. Chem.* xxviii. 192; Carleton-Williams, *Chem. Soc. Journ.* xxvii. 70; Mielek, *Lieb. Ann.* clxxx. 51; Bredt and Fittig, cc. 58.

the substance has a constant boiling-point, considered it to be a definite chemical compound. Bredt and Fittig, however, afterwards proved that it is a mixture of the lactone of oxyisocaproic acid with an acid, for which they retained the name of pyroterebic acid.[1] This latter is an oily liquid, possessing a characteristic, somewhat acrid, smell, solidifying at −15°, and being transformed, partly on distillation and completely on continued heating, into the isomeric lactone.[2] This remarkable change is explained by the following equation:



The characteristic calcium salt, $(C_6H_9O_2)_2Ca + 3H_2O$, crystallizes from hot water in glistening prisms.

Pyroterebic acid combines with bromine to form *dibromisocaproic acid*, $C_6H_{10}Br_2O_2$, forming large crystals melting at 99°—100°. According to Williams, acetic and isobutyric acids are formed on fusing crude pyroterebic acid with caustic potash.

751 *Ethyl-crotonic Acid*, $CH_3.CH{=}C(C_2H_5)CO_2H$. The ethyl salt of this acid is produced when diethyloxalic ether is heated with phosphorus trichloride. It is a liquid boiling at 165°, having at 13° a specific gravity of 0·9203, and smelling like peppermint.[3] This ethereal salt is also formed when diethyloxalic ether is treated with phosphorus pentachloride, and the chlordiethyl acetic ether, $(C_2H_5)_2CCl.CO_2C_2H_5$, thus produced, subjected to distillation.[4] By conversion into the potassium salt and distilling this with dilute sulphuric acid, the acid is obtained, which crystallizes from ether in oblique prisms, melts at 41°, and boils at 209°; it volatilizes, however, at the ordinary temperature and has an odour resembling that of benzoic acid. It is also produced by the distillation of ethyl-β-oxybutyric acid,[5] whilst it is a remarkable fact that the isomeric diethyloxalic acid when heated by itself does not yield ethyl-crotonic acid but an isomeric compound, a liquid boiling at 198°, and not solidifying at − 18°. Fuming hydrobromic acid converts this at once into ethyl crotonic acid, and the same change is produced on heating with

[1] *Lieb. Ann.* cc. 259. [2] *Ib.* Fittig and Geisler, *ib.* ccviii. 37.
[3] Frankland and Duppa, *Chem. Soc. Journ.* xviii. 133; Fittig and Howe, *Lieb. Ann.* cc. 21.
[4] Markownikoff and Drobjaskin, *Ber. Deutsch. Chem. Ges.* vi. 1175.
[5] Waldschmidt, *Ann. Chem. Pharm.* clxxxviii. 245.

dilute sulphuric acid or caustic potash,[1] whilst both acids when fused with the latter substance yield acetic and butyric acids. It seems probable, therefore, that the isomerism of these two acids is similar to that of crotonic and isocrotonic acids.

Ethyl-crotonic acid is not affected by sodium-amalgam and water. It combines slowly with concentrated hydrobromic acid, forming *bromhydro-ethyl-crotonic acid*, $C_6H_{11}BrO_2$, a crystalline mass melting at 25° and yielding with sodium-amalgam and water a fatty acid of the composition $C_6H_{12}O_2$. From its mode of formation this should be diethylacetic acid, but, as in some points it differs from this acid, Fittig and Howe have given to it the provisional name of *hydro-ethyl-crotonic acid*.

The brominated acid easily splits up in alkaline solution into carbon dioxide and *a*-methyl-ethyl-ethylene, a metallic bromide being at the same time formed.

Ethyl-crotonic acid combines with bromine to form *dibrom-hydro-ethyl-crotonic acid*, $C_6H_{10}Br_2O_2$, which separates from solution in carbon disulphide in large, transparent crystals, melting at 80°·5. When heated with water to 100°, brom-methyl-ethylene is formed, together with *hexeric acid*, $CH_3.CH(OH).C(OH)(C_2H_5).CO_2H$. This latter, which is an homologue of glyceric acid, dissolves readily in water, and crystallizes from ether in needles or rhombic prisms, melting at 141°.

*Methylethylacrolein*, $C_2H_5CH=C(CH_3)COH$, was obtained by Lieben and Zeisel by acting on propionaldehyde with a solution of sodium acetate. It is a liquid having a sharp penetrating odour, boiling at 137°, and combining with acid sodium sulphite to form a crystalline compound. With bromine it combines to form a dibromcaproic aldehyde.[2] When acted on by acetic acid and iron filings it yields, together with the corresponding alcohol, propyl-methyl alcohol and also the aldehyde of methyl-propyl-acetic acid. Hence its constitution is established, and its formation is as follows:

$$CH_3.CH_2.CHO + \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ COH \end{matrix} = CH_3.CH_2.CH=C\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ COH \end{matrix} + H_2O.$$

752 *Hydrosorbic Acid*, or *Propyl-acrylic Acid*, $CH_3.CH_2.CH_2.CH=CH.CO_2H$, is formed by the action of sodium-amalgam and

[1] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xii. 1354.
[2] *Monatsch. Chem.* iv. 1.

water on sorbic acid, $C_6H_8O_2$, which is obtained as a by-product in the preparation of malic acid from mountain-ash berries. It is a liquid, boiling at 208°, having at 19° a specific gravity of 0·969, and not solidifying in a freezing mixture.[1] On long-continued heating the boiling-point rises considerably, without, however, a product of constant boiling-point being obtained. An acid occurring in small quantity in croton oil is probably identical with hydrosorbic acid.[2]

On fusion with caustic potash, hydrosorbic acid splits up into acetic and normal butyric acids. It combines with bromine to form a liquid dibromcaproic acid, whilst sorbic acid combines with hydrobromic acid to form a dibromcaproic acid which forms large compact colourless transparent crystals, fusing at 68°. Hydrosorbic acid also combines readily with hydrobromic and hydriodic acids, forming substitution-products of normal caproic acids, which are converted into the latter by nascent hydrogen.

*Calcium Hydrosorbate*, $(C_6H_9O_2)_2Ca + H_2O$, crystallizes in concentrically-grouped needles, which dissolve more easily in cold than in hot water.

*Ethyl Hydrosorbate*, $C_6H_9O_2(C_2H_5)$, is a liquid having a fruit-like smell, and boiling at 166°—167°.

In addition to the acids above described, the following acids of this group are known :

| | | M.P. | B.P. |
|---|---|---|---|
| [3] Isopyroterebic acid, | Liquid. | — | 213°—215° |
| [4] Hexylenic acid, | Needles. | 39° | — |

753 *Teracrylic Acid*, $C_7H_{12}O_2$, is obtained by the dry distillation of terpentic acid, $C_8H_{12}O_4$, the latter being formed when oil of turpentine is oxidized with chromic acid. Teracrylic acid is an oily liquid, having an odour resembling, but pleasanter than, valeric and caproic acids. It boils at 218° and does not solidify in a freezing mixture. Its calcium salt, $(C_7H_{11}O_2)_2Ca + 5H_2O$, crystallizes in long prisms, which are readily soluble in cold water, but on heating with water fall to a powder, which dissolves again on cooling. When the acid is fused with caustic potash, the only fixed product is acetic acid, together with a small quantity of an acid that is non-volatile in a current of steam.

[1] Fittig and Barringer, *Ann. Chem. Pharm.* clxi. 309 ; Fittig, Stahl, Landsberg, and Engelhorn, *ib.* cc. 42.
[2] Schmidt and Berendes, *ib.* cxci. 121.
[3] Lagermark and Eltekow, *Journ. Russ. Chem. Ges.* xi. 125 ; *Ber. Deutsch. Chem. Ges.* xii. 854.
[4] Pinner, *Ber. Deutsch. Chem. Ges.* x. 1074.

When teracrylic acid is brought into contact with fuming hydrobromic acid, bromheptoic acid is first formed; this is, however, very unstable and quickly gives off hydrobromic acid, and yields

*heptolactone*, $C_6H_{12}\begin{cases}CO\\|\\O\end{cases}$

This is a colourless liquid, possessing a weak odour, boiling at 220°, and yielding when cooled a crystalline mass melting at 11°. At 0° it dissolves in 12 volumes of water; on warming, the solution becomes turbid, and at 30°—50° the liquid has a milky appearance, and the lactone separates out in part in oily drops, which dissolve again above 80°. On cooling again to 0° the same phenomena are observed in reverse order.

When the lactone is boiled with the hydroxides of the alkali metals or of metals of the alkaline earths, the salts of the corresponding *oxyheptylic acid*, $C_7H_{14}O_3$, are formed, but the acid itself does not exist in the free state.[1]

*Damaluric Acid*, isomeric with teracrylic acid, has been found by Städeler in the urine of man, of the horse, and of the cow (δάμαλις, heifer). It is an oily liquid, having a characteristic smell resembling that of valeric acid. The homologue *damolic acid*, $C_{12}H_{22}O_2$,[2] is also found with damaluric acid.

[1] Fittig and Krafft, *Lieb. Ann.* ccviii. 71.
[2] *Lieb. Ann.* lxxvii. 27.

## COMPOUNDS CONTAINING TEN TO FIFTEEN ATOMS OF CARBON.

754 Of these the following tertiary alcohols having the composition $C_8H_{16}O$, are known. They are obtained in a way similar to their lower homologues:

| | B.P. | Sp. Gr. at 0°. |
|---|---|---|
| [1] Allyl diethyl carbinol, $C_3H_5(C_2H_5)_2COH$ | 156° | 0·8891 |
| [2] Allyl methyl propyl carbinol, $C_3H_5(CH_3)(C_3H_7)COH$ | 159°—160° | 0·8486 |

### Alcohols having the Composition $C_{10}H_{20}O$.

| | | |
|---|---|---|
| [3] Allyl dipropyl carbinol, $C_3H_5(C_3H_7)_2COH$ | 192° | 0 8602 |
| [4] Allyl di-isopropyl carbinol, $C_3H_5[(CH_3)_2CH]_2COH$ | 169°—171° | 0 8671 |

### Amyldecatoic Acid, $C_{10}H_{18}O_2$.

755 The aldehyde of this acid is formed together with other condensation-products, when valeraldehyde is heated, either alone or with zinc clippings, to 240°, or when the acid is acted on with sodium, caustic potash, hydrochloric acid or potassium carbonate.[5] For its preparation valeraldehyde is boiled for some time with dry potassium carbonate, and the product subjected to fractional distillation.[6]

Amyldecaldehyde is an oil possessing a strong aromatic smell. It boils at 187°—191°, and at 0° has a specific gravity of 0·861.

[1] Saytzew and Schirokow, *Lieb. Ann.* cxcvi. 113.
[2] Zemilianicin, *Journ. Prakt. Chem.* [2], xxiii. 263.
[3] P. and A. Saytzew, *Lieb. Ann.* cxcvi. 109.
[4] Lebedinsky, *Journ. Prakt. Chem* [2], xxiii. 23.
[5] Borodin, *Ber. Deutsch. Chem. Ges.* ii. 552; v. 480; Riban, *Bull. Soc. Chim.* [2], xiii. 24; Kekulé, *Ber. Deutsch. Chem. Ges.* iii. 135.
[6] Gäss and Hell, *ib.* viii. 371.

By oxidation the aldehyde is transformed into amyldecatoic acid, which has already been described as isocapric acid (Part I. p. 665). Borodin has, however, found that it belongs to the acrylic series, whence it follows that the so-called isocapric alcohol (Part I. p. 665) is an homologue of allyl alcohol and has the formula $C_{10}H_{20}O$.

Amyldecatoic acid is an oily liquid, boiling at 241°·5 and at 0° having a specific gravity of 0·9096. It combines with bromine forming dibromcapric acid, $C_{10}H_{18}Br_2O_2$, which crystallizes in glistening monoclinic prisms, melting at 135°.[1]

*Amenyl-valeric Acid*, $C_{10}H_{18}O_2$, was obtained by Fröhlich and Geuther, together with other products, by the action of carbon monoxide on sodium amylate at 210°. It is a thick oily liquid, possessing a characteristic smell, and boiling at 268°—270°.[2]

*Undecylenic Acid*, $C_{11}H_{20}O_2$, is formed, together with œnanthol, when castor-oil is distilled under reduced pressure (Part I. p. 647). It forms a crystalline mass melting at 24°·5. Under ordinary pressure, it boils with slight decomposition at 295°, but distils unchanged under a pressure of 90 mm. at 198°—200°. It combines with bromine, forming *dibromundecylic acid*, $C_{11}H_{20}Br_2O_2$, and on heating with hydriodic acid is transformed into undecylic acid (Part I. p. 667). When fused with caustic potash it splits up into acetic and nonoic acid, whilst fuming nitric acid oxidizes it to sebacic acid.[3]

*Cimicic Acid*, $C_{15}H_{28}O_2$, is contained in the exceedingly disagreeably smelling liquid, ejected as a defence by the grey leaf-bug (*Rhapigaster puncti pennis*) belonging to the genus cimex. It crystallizes from ether in prisms united in stellar forms, melts at 44°, and is difficultly soluble in alcohol.[4]

## THE OLEIC ACIDS.

**756** The higher members of this group of acids occur as glycerides in various oils and fats. They do not volatilize without decomposition, and are distinguished from the corresponding fatty acids, inasmuch as their lead salts are soluble in ether. Another characteristic reaction is that they are transformed by a small

[1] Hell and Schoop, *Ber. Deutsch. Chem. Ges.* xii. 193.
[2] *Lieb. Ann.* ccii. 294.
[3] Krafft, *Ber. Deutsch. Chem. Ges.* x. 1034; Becker, *ib.* xi. 1412.
[4] Carius, *Ann. Chem. Pharm.* cxiv. 147.

quantity of nitrogen trioxide into isomeric acids possessing a higher melting point. Their glycerides, also, undergo a similar change; and this explains why oil of almonds, olive oil, &c., solidify when treated with nitrogen trioxide.

*Hypogæic Acid*, $C_{16}H_{30}O_2$, was found by Gössmann and Scheven, together with palmitic and arachidic acid in earth-nut oil,[1] which is used as a substitute for olive oil, and is obtained from the seeds of *Arachis hypogæa*. Hypogæic acid may be prepared by decomposition of the lead salt; or the oil is saponified with weak soda ley, the free acids extracted from the soap, and these dissolved in the smallest possible quantity of hot alcohol. On cooling, part of the fatty acids separate out. The filtrate is evaporated in hydrogen, and the residue treated again as above until no further separation of crystals occurs on cooling, and the solution is then evaporated.[2] Hypogæic acid forms colourless needle-shaped crystals, which melt at 33° and dissolve very readily in alcohol. It combines with a molecule of bromine, and is converted in contact with nitrogen trioxide,[3] or by heating with common nitric acid (Schröder), into *gaeïdinic acid*, a crystalline mass, which melts at 39°, is readily soluble in alcohol, and, like its isomeride, combines with bromine.

Isomeric with these acids, also, is *physetoleic acid*, which is contained in the spermaceti oil found in cavities in the head of the sperm-whale (*Physeter macrocephalus*). This melts at 30°,[4] and on distillation does not yield sebacic acid, as is the case with hypogæic acid (Caldwell and Gössmann).

757 *Oleic Acid*, $C_{18}H_{34}O_2$. This acid was discovered by Chevreul, although Gottlieb first obtained it in the perfectly pure state, and ascertained its formula.[5] It occurs as triolein in most liquid and solid fats, such as non-drying oil, almond oil, olive oil, cod-liver oil, &c., being contained in these bodies in large quantities, and it is also found in the fat of the goose, as well as in lard. The acid obtained from the latter was considered by Bromeis to be a distinct one,[6] but Gottlieb and Heintz showed that it is identical with oleic acid.[7] This is also the case with the benic acid found by Walter in behen-oil (*Moringa aptera*) and to which he gave the formula of $C_{15}H_{18}O_2$,[8] but Zalesky showed that this

[1] *Ann. Chem. Pharm.* xciv. 230.
[2] Schröder, *Ann. Chem. Pharm.* cxliii. 22.
[3] Caldwell and Gössmann, *ib.* xcix. 307.
[4] Hofstädter, *Ann. Chem. Pharm.* xci. 177.
[5] *Ib.* lvii. 38. [6] *Ann. Chem. Pharm.* xlii. 55.
[7] *Pogg. Ann.* lxxxiii. 555; lxxxix. 583; xc. 143.
[8] *Ann. Chem. Pharm.* lx. 271.

is impure oleic acid.[1] Oleic acid also exists in the different varieties of tallow and other solid fats, and is obtained in large quantities as a by-product in the manufacture of stearin candles.

Gottlieb obtained the pure acid by saponifying almond oil with potash solution, decomposing the soap with hydrochloric acid, and heating the resulting mixture of acids with lead oxide for some hours to 100°. From the mixture of lead salts thus obtained, the lead oleate is separated by exhaustion with ether, and the solution is then shaken up with hydrochloric acid. Impure oleic acid is obtained from the filtrate by evaporating off the ether. This acid is dissolved in ammonia, and a solution of barium chloride added, when barium oleate is precipitated, and this is purified by recrystallization from alcohol, and then decomposed by tartaric acid.

Olive oil, lard, or commercial oleic acid, may be used instead of almond oil, and the acid separated from the lead salt may be purified by cooling to between −6 and −7, when the acid crystallizes; the liquid impurities are removed by subjecting to strong pressure, and these operations of cooling and pressing repeated until a pure product is obtained (Bromeis).

If the commercial oleic acid has been recently prepared, and therefore contains but little products of oxidation, it is cooled down to 0° in order to separate stearic and oleic acids; the liquid is pressed out, and then by the process last described a tolerably pure acid may be obtained.

*Properties.* Oleic acid is a colourless oil, which on cooling solidifies to brilliant, colourless, and tasteless needles melting at 14°. Their alcoholic solution, when pure, has a neutral reaction (Gottlieb). Pure oleic acid is moderately stable, but the impure acid readily absorbs oxygen, becomes yellow coloured, and acquires an acid reaction and rancid odour.

When heated with amorphous phosphorus and fuming hydriodic acid to 200°—210°, it is converted into stearic acid.[2] On fusion with caustic potash it splits up into acetic and palmitic acids.[3] This reaction is now used for the preparation of the latter acid on the large scale.[4] Nitric acid oxidizes it with formation of acids of the fatty and of the oxalic series, and on dry distillation it yields acetic, caprylic, capric, and sebacic acids, hydrocarbons and carbon dioxide. It may, however,

[1] *Ber. Deutsch. Chem. Ges.* vii. 1013. [2] Goldschmidt, *Jahresb.* 1876, 579.
[3] Varrentrapp, *Ann. Chem. Pharm.* xxxv. 196.
[4] Carpenter, *Journ. Soc. Chem. Ind.* ii. 98.

be distilled in a current of superheated steam at 250° without decomposition.[1] It combines with bromine to form a dibromstearic acid, $C_{18}H_{34}Br_2O_2$, a thick yellow oil, having a fruit-like odour.[2]

*Sodium Oleate*, $C_{18}H_{33}NaO_2$, is a constituent of hard soap (Part I. p. 690). The salt prepared from pure oleic acid can be crystallized from absolute alcohol, but not from aqueous alcohol or from the syrupy solution in water (Varrentrapp). The *potassium* salt forms a transparent jelly, and is decomposed by a large quantity of water into caustic potash and the insoluble acid salt. *Barium Oleate*, $(C_{18}H_{33}O_2)_2Ba$, is insoluble in water, difficultly soluble in boiling spirit, and forms a snow-white, light, crystalline powder. *Lead Oleate*, $(C_{18}H_{33}O_2)_2Pb$, is a light, white powder, which melts at 80° to a yellow oil, and this on cooling forms a brittle, translucent mass.

758 The *glycerides* of oleic acid were obtained by Berthelot by a method similar to that employed in the preparation of the glycerides of the fatty acids.[3] *Monolein* and *diolein* are oily liquids, which on cooling solidify to a crystalline mass.

*Triolein*, $(C_{18}H_{33}O_2)_3C_3H_5$, is obtained by heating glycerol with an excess of oleic acid to 240°. It may also be prepared from almond oil or olive oil, by cooling down to 0°, removing the liquid part from the glycerides of the fatty acids by pressure, and dissolving in three times its volume of hot alcohol, and again cooling down to 0°, or, better, a few degrees below 0°, when still more of the glycerides separate out. The alcohol is then distilled off, and the residue washed free from adhering alcohol by water. A still purer triolein is obtained, according to Kerwyck, from cold-pressed olive oil by allowing it to stand twenty-four hours over caustic soda solution, with frequent shaking, by which means the glycerides of the fatty acids are chiefly saponified. The soap thus produced is removed by dilute alcohol, and the triolein, which has the usual yellow colour, is then decolorized by animal charcoal.[4]

Triolein is an oily neutral liquid devoid of taste and smell. It can be distilled in a vacuum, and solidifies below 0°. When exposed to the air it takes up oxygen and becomes acid and rancid.

Oleic acid dissolves in concentrated sulphuric acid to a colourless solution, a sulphonic acid being formed. This was termed

[1] Bolley and Borgmann, *Zeitsch. Chem.* 1866, 187.
[2] Burg, *Journ. Prakt. Chem.* xciii. 227 ; Overbeck, *Ann. Chem. Pharm.* cxl. 43.
[3] *Ann. Chim. Phys.* [3], xli 243. [4] Kolbe-Meyer, *Lehrb. Org. Chem.* ii. 25.

by Fremy *olein-sulphuric acid*, but he did not succeed in obtaining it pure. He found also that when two parts of olive oil and one part of sulphuric acid are brought together, the mixture being well cooled, and after twenty-four hours decomposed with water, an oily layer separates, which consists of the sulphonic acids of oleic acid and margaric acid (palmitic and stearic acids), whilst the aqueous solution contains the excess of sulphuric acid and glycerol-sulphuric acid.[1] Mercer and Greenwood long ago proposed the use of this sulpho-acid in place of olive oil in the Turkey-red industry, and, later, John Lightfoot introduced the use of the sodium salt in calico-printing, as a "prepare" for cloth for steam colours, the effect being to heighten and brighten the tints.[2]

Lightfoot stated that other oils may also be used for this purpose, and at the present day castor oil is much used.

759 *Elaïdic Acid.* Boyle, in 1661, mentions that olive oil and almond oil both become thick when acted upon by fuming aqua fortis, and other chemists observed that nitrous vapours produce the same effect. These observations were, however, entirely forgotten until a Marseilles apothecary, Poutet, noticed in 1819 that olive oil becomes solid when shaken up with a solution of mercury in nitric acid,[3] and on this observation he founded a method for detecting the adulteration of olive oil with foreign oils; but, later, Boudet and Lescalier pointed out that other oils also give a similar reaction with the mercury solution, and that this cannot be used for the detection of adulteration in olive oil. Felix Boudet, following up Poutet's observation, found that the mercury solution only acts as described when it contains free nitrous acid. He further established the fact that a new body is formed in this reaction, and to it he gave the name of *elaïdin*, and this he considered to be a compound of glyceryl oxide with a new acid which he termed *elaïdic acid*.[4] This was then further examined by Laurent,[5] Boudet and Pelouze,[6] and Meyer,[7] the last-named preparing it from oleic acid. Its correct formula was, however, first established by Gottlieb.[8]

For its preparation, nitrous fumes are passed for a few minutes into pure oleic acid which is kept cold, and this in about half

[1] *Ann. Chim. Phys.* [2], lxv. 113.
[2] Patent No. 769, 1864.
[3] *Ann. Chim. Phys.* xii. 58.
[4] *Ann. Chem. Pharm.* iv. 1.
[5] *Ib.* xxviii. 253; *Ann. Chim. Phys.* lxv. 294.
[6] *Ann. Chem. Pharm.* xxix. 41.
[7] *Ib.* xxxv. 174.
[8] *Ib.* lvii. 52.

an hour solidifies to a mass consisting of large plates. This is then washed with boiling water and purified by recrystallization from alcohol. It crystallizes in large pearly plates, resembling benzoic acid, melts at 44°—45°, and at a higher temperature distils, almost without decomposition. It has a strongly acid reaction, combines readily with bromine, and when fused with caustic potash splits up into acetic and palmitic acids (Meyer, Varrentrapp), whilst, when heated with phosphorus and hydriodic acid, it is transformed into stearic acid (Goldschmidt).

In the fused state it quickly absorbs oxygen, and in the course of a couple of weeks 65 per cent. of it is changed into a semi-fluid yellow mass, smelling of poppy-oil.

Since solid elaïdic acid is so readily obtained from liquid oleic acid, it has been proposed to prepare it on the large scale for making candles, but the idea has not as yet been practically carried out.[1]

*Sodium Elaïdate*, $C_{18}H_{33}NaO_2$, crystallizes from alcohol in light laminæ, having a silvery lustre. Its dilute aqueous solution becomes turbid and alkaline on standing, scales of the acid salt separating out (Boudet, Laurent, Meyer). The *potassium* salt forms glistening needles (Boudet); the *barium* salt and the *lead* salt are white precipitates (Meyer).

By heating silver bromstearate with water, Oudemanns obtained an acid which is isomeric with elaïdic acid, but dissolves more readily in alcohol. It forms an amorphous mass, melting at 35°.[2]

760 *Doeglic Acid*, $C_{19}H_{36}O_2$. The glyceride of this acid forms, according to Scharling, the principal part of the doegling train-oil (from the bottle-nosed whale, *Balaena rostrata*). The acid is a yellow oil, which solidifies on cooling.[3]

*Erucic Acid*, $C_{22}H_{42}O_2$, occurs in the fatty oil of white and black mustard,[4] in rape-seed oil,[5] and in grape-seed oil.[6] For its preparation the rape-seed oil is boiled with water and lead oxide, and the lead-soap extracted with cold ether, when the solution contains chiefly an acid which has not been closely examined, and to which the name sinoleic acid has been given.[7] The residual lead salt is decomposed with alcoholic hydrochloric acid. Erucic acid forms long thin glistening needles, which

[1] *Ber. Entw. Chem. Ind.* ii. 499.
[2] *Journ. Prakt. Chem.* lxxxix. 193.
[3] *Journ. Prakt. Chem.* xliii. 257.
[4] Darby, *Ann. Chem. Pharm.* lxix. 1.
[5] Websky, *Journ. Prakt. Chem.* lviii. 449.
[6] Fitz, *Ber. Deutsch. Chem. Ges.* iv. 442.
[7] Darby; Städeler, *Ann Chem Pharm* lxxxvii. 153.

melt at 34°. When fused with potash it splits up into arachic acid and acetic acid. Nitrogen trioxide or dilute nitric acid[1] transforms it into *brassidic* or *erucidic acid*, which crystallizes from alcohol in laminæ which melt at 56°. On heating with hydriodic acid and phosphorus, it is reduced, as is also erucic acid, to behenic acid, $C_{22}H_{44}O_2$ (Goldschmidt).

## Ricinoleic Acid, $C_{18}H_{34}O_3$.

761 This acid, although it does not belong to the foregoing group, is intimately connected with it. It occurs as glyceride in castor oil,[2] together with small quantities of tripalmitin and tristearin, and in the oil obtained from the seeds of *Jatropha Curcas* (*Curcas purgans*).[3] It is prepared from castor oil by a process similar to that by which oleic acid is obtained from olive oil;[4] or more simply, castor-oil soap is fractionally precipitated by means of calcium chloride, the first fraction (about one-third of the whole) set aside, and the later fractions twice crystallized from alcohol. A pure calcium ricinoleate is thus obtained, which is then decomposed with hydrochloric acid.[5]

Ricinoleic acid is a thick oily liquid, which solidifies below 0°, and mixes in every proportion with alcohol and ether. Its alcoholic solution has an acid reaction, an unpleasant persistent acrid taste, and it does not oxidize in the air. As has already been described, it decomposes on heating with alkalis, into methylhexyl carbinol and sebacic acid, and on distillation under diminished pressure yields œnanthol and undecylic acid. It combines with bromine, and when acted on with iodine, phosphorus and water, is transformed into *iodstearidic acid*, $C_{18}H_{33}IO_2$, a yellow oil, which on heating with hydrochloric acid and zinc filings yields stearic acid (Claus and Hassenkamp).

When castor oil is treated with alcoholic ammonia, *ricinolamide*, $C_{18}H_{33}O_2(NH_2)$ is formed;[6] it is a white crystalline mass which melts at 66°, and is decomposed by hydrochloric acid into ricinoleic acid and sal-ammoniac.[7]

[1] Haussknecht, *Ann. Chem. Pharm.* cxliii. 41.
[2] Bussy and Lecanu, *Journ. Pharm.* xiii. 57.
[3] Bouis, *Compt. Rend.* xxxix. 923; Arnaudon and Ubaldini, *Jahresb.* 1858, 536; Silva, *Compt. Rend* lxvii. 1261.
[4] Saalmüller, *Ann. Chem. Pharm.* lxiv. 108; Svanberg and Kolmodin, *Journ. Prakt. Chem.* xlv. 431.
[5] Claus and Hassenkamp, *Ber. Deutsch. Chem. Ges.* ix. 1961.
[6] Boullay, *Compt. Rend.* xxxii. 223.
[7] Bouis, *Ann. Chim. Phys.* [3], xliv. 96.

On dissolving castor oil in sulphuric acid a sulphonic acid is produced. A solution of its ammonium salt mixed with that of sulphopyroterebic acid is used in commerce under the name of Turkey-red oil, and is used in Turkey-red dyeing and in calico-printing. Castor oil also dissolves readily in soda-ley, and such a solution, known in commerce as "soluble oil," is used as a "prepare" in calico-printing. Castor oil is likewise used in the manufacture of soap.

*Ricinelaïdic Acid* is obtained by the action of nitrogen trioxide on ricinoleic acid,[1] and is also produced when this acid is heated with ordinary nitric acid.[2] It crystallizes from alcohol in silky glistening needles united in tufts, which melt at 50°. With bromine and caustic soda it exhibits reactions corresponding to those of ricinoleic acid.[3]

## TRIBASIC ACIDS, $C_nH_{2n-1}(CO_2H)_3$, AND COMPOUNDS RELATED THERETO.

762 *Methenyl-Tricarboxylic Acid*, $CH(CO_2H)_3$, is not known in the free state. Its ethyl salt is obtained by the action of ethyl chloroformiate (ethyl chlorcarboxylate) on pure sodium malonic ether. It is a pleasantly-smelling liquid, which distils between 254° and 260°, and is decomposed by potash solution with formation of potassium malonate, potassium carbonate, and alcohol.[4]

*Ethenyl Tricarboxylic Acid*, $C_2H_3(CO_2H)_3$, is obtained in a similar way from ethyl chloracetate:

$$\begin{array}{l} CO_2.C_2H_5 \\ | \\ CHNa \\ | \\ CO_2.C_2H_5 \end{array} + ClCH_2.CO_2.C_2H_5 = \begin{array}{l} CO_2.C_2H_5 \\ | \\ CH.CH_2.CO_2.C_2H_5 \\ | \\ CO_2.C_2H_5 \end{array} + NaCl.$$

The ethereal salt thus obtained is a liquid boiling at 275°—280°. The acid prepared from it crystallizes in colourless prisms, fusing at 159°,[5] with evolution of carbon dioxide, and when the heat is continued sufficiently long only succinic acid is left behind.

[1] Boudet, Playfair, *Ann. Chem. Pharm.* lx. 322.
[2] Ulrich, *Zeitsch. Chem.* 1867, 548.
[3] Koch, *Ann. Chem. Pharm.* cxix. 174.
[4] Conrad. *Ber. Deutsch. Chem. Ges.* xii. 752.
[5] Bischoff, *Ann. Chem. Pharm.* ccxiv. 68.

The same acid is obtained when ethyl chlormalonate acts upon ethyl iodomalonate, *acetylene-tetracarboxylic acid*, $C_2H_2(CO_2H)_4$, being produced:[1]

$$\begin{matrix} C_2H_5.CO_2 \\ C_2H_5.CO_2 \end{matrix}\!\!>\!CHCl + NaHC\!<\!\begin{matrix} CO_2.C_2H_5 \\ CO_2.C_2H_5 \end{matrix} =$$

$$\begin{matrix} C_2H_5.CO_2 \\ C_2H_5.CO_2 \end{matrix}\!\!>\!CH\!-\!CH\!<\!\begin{matrix} CO_2.C_2H_5 \\ CO_2.C_2H_5 \end{matrix} + NaCl.$$

This ethereal salt forms glistening white needles, which melt at 76°. It boils at 305°, and is decomposed by potash solution with formation of ethenyl-tricarboxylic acid.

By the action of chlorine on the ethyl salt of this acid, *ethyl monochlorethenyl-tricarboxylate*, $C_2H_2Cl(CO_2.C_2H_5)_3$, is obtained, which boils with partial decomposition at 290°, and by prolonged heating with hydrochloric acid is transformed into fumaric acid:

$$\begin{matrix} CH_2.CO_2.C_2H_5 \\ | \\ CCl(CO_2.C_2H_5)_2 \end{matrix} + 3H_2O = \begin{matrix} CH.CO_2H \\ \| \\ CH.CO_2H \end{matrix} +$$

$$CO_2 + HCl + 3C_2H_5OH.$$

When the chlorinated ethyl salt is saponified with potash, inactive malic acid is produced, identical with that obtained by Loydl from fumaric acid.[2]

By the action of sodium ethylate and propyl iodide on the ethyl salt of ethenyl-tricarboxylic acid it is converted into the ethyl salt of *propyl-ethenyl-tricarboxylic acid*, $C_3H_7(CO_2H)_2CH_2.CO_2H$, which boils with decomposition at 280°. The acid obtained from this, crystallizes in glistening needles, which melt at 148° and decompose when further heated into propyl-succinic acid and carbon dioxide.[3]

*β-Methyl-ethenyl Tricarboxylic Acid*, $CH_3.CH(CO_2H)CH(CO_2H)_2$, The ethyl salt of this acid is obtained by acting with ethyl brompropionate on ethyl sodomalonate, and is a liquid which boils at 270°, and is readily saponified by potash solution. The free acid forms a glistening crystalline mass, which melts at

[1] Conrad and Bischoff, *Ann. Chem. Pharm.* ccxiv. 68.
[2] Bischoff, *Ann. Chem. Pharm.* ccxv. 44.
[3] Waltz, *ib.* ccxiv. 58.

142°, and on longer heating splits up into pyrotartaric acid and carbon dioxide.[1]

763 *Desoxalic Acid,* or *Dioxyethenyltricarboxylic Acid,* $C_2H(OH)_2(CO_2H)_3$, was discovered in 1861 by Löwig, who obtained its ethyl salt by the action of sodium-amalgam on ethyl oxalate, and from this he prepared the free acid. He pointed out that its solution splits up on heating into racemic acid and carbon dioxide, this forming the first instance of the synthesis of a higher organic acid by reduction of oxalic acid. In this reaction other products are obtained in addition to ethyl desoxalate. Amongst these Löwig noticed a substance which possesses a sweet taste, is decomposed by means of yeast into alcohol and carbon dioxide, and also exhibits other properties characteristic of an optically active sugar, but he did not examine it further.[2]

According to Brunner the first action of sodium-amalgam on ethyl oxalate is to produce the ethyl salt of an acid having the composition $C_6H_8O_9$, and the solution of this on evaporation decomposes into racemic acid and glyoxylic acid, whilst when the ethyl salt is saponified with potash solution or the potassium salt is decomposed with acetic acid, Löwig's acid is formed.[3] Klein was, however, unable to confirm these observations, but obtained the same results as Löwig.[4]

To prepare desoxalic acid, equal volumes of a three per-cent. sodium amalgam and of ethyl oxalate are brought into a cylinder, kept cold by water, and shaken together frequently. The product is exhausted with ether, and the solution shaken up with small quantities of water. The ether is then distilled off and the residue allowed to stand until the ethyl desoxalate has crystallized out. This is then decomposed with potash solution, the solution rendered faintly acid with nitric acid, and then precipitated with lead nitrate. The washed lead salt is decomposed with sulphuretted hydrogen and the solution of the acid thus obtained is evaporated over sulphuric acid.

Desoxalic acid crystallizes with one molecule of water of crystallization. It is very deliquescent and dissolves readily in alcohol. When its aqueous solution is heated to 45°, it evolves carbon dioxide, and this decomposition proceeds rapidly when

[1] Bischoff, *Ber. Deutsch. Chem. Ges.* xiii. 2165 ; Bischoff and Guthzeit, *ib.* xiv. 614.
[2] *Journ. Prakt. Chem.* lxxxiii. 129 ; lxxxiv. 1.
[3] *Ber. Deutsch. Chem. Ges.* iii. 974 ; xii. 542.
[4] *Journ. Prakt. Chem.* [2], xx. 146.

the liquid is boiled, an acid being formed which has been supposed to be racemic acid, but which is doubtless the very similar glycotartaric acid :

$$\begin{matrix} CH(OH)CO_2H \\ | \\ C(OH)(CO_2H)_2 \end{matrix} = CO_2 + \begin{matrix} CH(OH)CO_2H \\ | \\ CH(OH)CO_2H. \end{matrix}$$

*Normal Potassium Desoxalate*, $C_5H_3O_8K_3$, remains on evaporating its solution as a gum-like mass, which on standing over sulphuric acid becomes crystalline. When its solution is supersaturated with acetic acid, the acid salt, $C_5H_4O_8K_2$, separates out after some time in brilliant, white, hard, crystalline crusts.

The desoxalates of calcium, barium, lead, and silver are white precipitates.

*Ethyl Desoxalate*, $C_5H_3O_8(C_2H_5)_3$, separates from its solution in warm water in large glistening triclinic crystals, which melt at 85°, are odourless, and have a purely bitter taste. When heated for some time to 140°—150° it is converted into an oily liquid which does not solidify on cooling, and has an exceedingly bitter taste. This modification is also contained in the mother-liquor from the crystals which have been deposited. On treatment with bases it yields salts identical with those prepared from the crystalline variety.

When heated with acetic anhydride, *ethyl diacetyl-desoxalate*, $C_2H(O.C_2H_3O)_2(CO_2.C_2H_5)_3$, is obtained, as an oily liquid possessing a very bitter taste.

764 *Propenyl Tricarboxylic Acid*, $C_3H_5(CO_2H)_3$, was first obtained by Dessaignes[1] by the action of nascent hydrogen on aconitic acid, $C_3H_3(CO_2H)_3$. Soon afterwards Maxwell Simpson prepared an acid of the same composition synthetically, by converting propenyl tribromide into the corresponding cyanide, and decomposing this by heating with potash solution.[2] Kekulé put forward the supposition that Simpson's acid is identical with that of Dessaignes, and termed it *carballylic acid*. Wichelhaus then proved the correctness of Kekulé's view,[3] and Simpson, who investigated the acid more closely, altered its name to *tricarballylic* acid.[4]

This acid is also formed when allylene dichloride, $C_3H_4Cl_2$, is heated with alcohol and potassium cyanide and the product

[1] *Ann. Chem. Pharm.* Suppl. ii. 188.
[2] *Ann. Chem. Pharm.* cxxviii. 351.
[3] *Ib.* cxxxii. 61.
[4] *Ib.* cxxxvi. 272.

decomposed with potash,[1] and it may be obtained in the same way from the ethyl salt of chlorcrotonic acid.[2] It is obtained, further, by means of the acetoacetic ether reaction. When the sodacetacetate is treated with ethyl chloracetate, ethylacetosuccinate (p. 189) is formed, and the sodium compound of this is transformed by ethyl chloracetate into *ethyl acetotricarballylate*, $CH_3.CO.C_3H_4(CO_2.C_2H_5)_3$. This is a liquid which is readily decomposed by caustic potash or baryta-water as follows:[3]

$$\begin{array}{l} \quad CH_2.CO_2.C_2H_5 \\ CH_3.CO.C.CO_2.C_2H_5 \\ \quad CH_2.CO_2.C_2H_5 \end{array} + 4KOH = CH_2.CO.OK + \begin{array}{l} CH_2.CO_2K \\ CH.CO_2K \\ CH_2.CO_2K \end{array} + 3C_2H_5.OH.$$

The above-mentioned ethereal salt of ethenyltricarboxylic acid (p. 425) contains an atom of hydrogen which is replaceable by sodium; if the sodium compound be then treated with ethyl chloracetate, the salt of *isoallylene-tetracarboxylic acid*, $C_3H_4(CO_2H)_4$, is obtained, which crystallizes in large prisms, and decomposes at 151° into tricarballylic acid and carbon dioxide:[4]

$$\begin{array}{l} CH_2.CO_2H \\ C\begin{array}{l}\diagup CO_2H \\ \diagdown CO_2H\end{array} \\ CH_2.CO_2H \end{array} = \begin{array}{l} CH_2.CO_2H \\ CH.CO_2H \\ CH_2.CO_2H \end{array} + CO_2.$$

Tricarballylic acid is frequently found as calcium salt, together with aconitic acid and citric acid, $C_3H_4(OH)(CO_2H)_3$, in the deposit in the stills used in beet-sugar works.[5]

It forms rhombic crystals readily soluble in water and alcohol, and melting at 158°. It is not attacked by nitric acid, and on heating part of it sublimes without decomposition.

[1] Claus, *ib.* clxx. 131.
[2] Claus, *ib.* cxci. 63.
[3] Miehle, *Ann. Chem. Pharm.* cxc. 322.
[4] Conrad, *Ber. Deutsch. Chem. Ges.* xiii. 2163.
[5] Von Lippmann, *Ber. Deutsch. Chem. Ges.* xi. 707; xii. 1649.

## CITRIC ACID, $C_6H_8O_7$.

765 The acid contained in lemon juice, the existence of which must have been noticed in very early times, was first distinctly mentioned by a chemist in the thirteenth century. In his *Speculum Naturale* Vincentius Bellovacensis says: "*Solutiva corporum multa sunt, ut aqua limonum, vel pomorum citrinorum, quæ dicuntur melangoli, vel orangii, distillata per filtrum.*" Boerhave also refers to it as a solvent in his *Elementa Chemiae*, in 1732, where he states that many very powerful vegetable solvents or acids exist, "*quum succus recens aurantii, citrei limonii, plumbum, stannum, cuprum, ferrum dissolvat, satisque fortiter calcinare queat, acque quam fossila acida.*" N. Lemery believed that this acid was identical with that of the grape, for he asserts that in the preparation of the "*extrait de mars aperitif*" made from iron-rust, water, and new wine or lemon-juice, it is "*les sucs tartareux du raisin et des limons*" which produce the desired effect. Stahl considered this acid to be acetic acid, but Retzius, in 1776 pointed out that it differs from this, inasmuch as the lead salt is insoluble in water, whilst it differs from tartaric acid, in that it does not form a sparingly soluble potassium salt. He did not however obtain the acid in the form of crystals, which was first accomplished by Scheele in 1784.

Citric acid is found widely distributed in nature. According to Scheele it occurs in the free state, and accompanied with little or no malic acid in the lemon, orange, sloe, cranberry, whortleberry, hipberry, and in the berries of *Solanum dulcamara*, and also, according to Stein, in *Drosera intermedia*.[1] Together with about an equal quantity of malic acid it is found in the gooseberry, currant, bilberry, raspberry, strawberry, and cherry, whilst the tamarind (Vauquelin) and the mountain-ash berry (Liebig) contain both these acids together with tartaric acid.

The citrates of calcium and potassium are also very widely distributed in the vegetable kingdom; amongst the well-known plants in which they occur, may be mentioned: in the haulm of *Aconitum lycoctonum*, *Convallaria majalis*, *Isatis tinctorum*, in the tobacco plant, in the milky juice of lettuce, and in the tubers of the Jerusalem artichoke and dahlia, the potato, onion, beetroot, &c.

[1] *Ber. Deutsch. Chem. Ges.* xii 1603.

*Preparation.* Citric acid is principally obtained from lemon juice, which forms a considerable article of export from the Italian and Spanish ports, as well as from Sicily, the West Indies, and the Sandwich Islands. It is also obtained from the several species of lemons, viz., *Citrus medica*, *C. Limonum*, and *C. Bergamia*, the rind of these fruits being utilised for the preparation of the ethereal oil. The juice ferments when allowed to stand, a deposit forming which is separated by filtration. The juice contains from 6 to 7 per cent. of citric acid, and is not only used to manufacture citric acid, but without further treatment, is employed as an excellent anti-scorbutic. The inspissated juice, containing about 23 per cent. of acid, also forms an article of commerce.

Citric acid is still manufactured from this juice according to the method originally suggested by Scheele. The lemon-juice, heated almost to the boiling-point, is treated with finely powdered chalk until no further evolution of carbonic acid occurs, when milk of lime is added. The calcium citrate thus precipitated is washed with boiling water until the filtrate is colourless. Calcium citrate is also frequently prepared in this way from the fresh juice in districts where lemons are plentiful, and then brought into commerce.[1] To obtain the acid, this salt is decomposed by the calculated quantity of sulphuric acid, the solution concentrated to the crystallizing point, and the acid thus obtained purified by recrystallization.

Tilloy has proposed to prepare citric acid from currants. The juice is first allowed to ferment, the alcohol is then distilled off, and the residual liquor worked up for the acid by the method above described. One hundred kilograms of currants yield one kilogram of citric acid and ten liters of alcohol of about 40 per cent.[2] According to Gräger, cranberries may be treated in a similar way for the preparation of both citric acid and alcohol.[3]

766 *Synthesis.* Citric acid can also be prepared synthetically, and its synthesis serves as an excellent example of the statement that any compound occurring in the organic world can be artificially prepared so soon as its constitution is known (Part I. p. 10). The first step towards a knowledge of its constitution was made by Liebig, who rightly fixed the molecular weight of the acid, and pointed out that it is tribasic.[4] Or heating, it loses a molecule of water and is transformed into aconitic acid, $C_6H_6O_6$, which is also

[1] *Ber. Entw. Chem. Ind.* ii. 425.
[2] *Journ. Pharm.* [2], xiii. 305.
[3] *Neu. Jahrb. Pharm.* xxxix. 193.
[4] *Ann. Chem. Pharm.* xxvi. 151.

tribasic. Hence it follows that it contains an hydroxyl in addition to three carboxyl groups, and this is also shown by the fact that it contains a hydrogen atom easily replaceable by an acid radical. From these observations the rational formula, $C_3H_4(OH)(CO_2H)_3$, was deduced. Aconitic acid combines with hydrogen, forming tricarballylic acid, $C_3H_5(CO_2H)_3$, which has also been prepared from propenyl tribromide by the replacement of the bromine by carboxyl, and this fixes its constitution. Citric acid is, however, the corresponding oxyacid, and can exist in two forms :

$$\begin{array}{l} CH_2.CO_2H \\ | \\ C(OH).CO_2H \\ | \\ CH_2.CO_2H \end{array} \qquad \begin{array}{l} CH_2CO_2H \\ | \\ CH.CO_2H \\ | \\ CH(OH).CO_2H. \end{array}$$

The first of these seems to be the most probable formula for citric acid, since it often yields as a decomposition product, acetone, or some of its derivatives. The correctness of this view has been established by the researches of Grimaux and Adam. Starting from dichlorhydrin, and oxidizing this to dichloracetone, they then combined this with hydrocyanic acid, and obtained *dichloroxyisobutyronitril*, $CH_2Cl.C(OH)(CN)CH_2Cl$, and this latter on decomposition with hydrochloric acid, was transformed into the corresponding acid. The potassium salt of this acid was then heated with a concentrated solution of potassium cyanide, and converted into a salt of *dicyanoxyisobutyric acid*, and this product, when saturated by hydrochloric acid and heated, yielded citric acid.[1]

767 *Properties.* Citric acid crystallizes with one molecule of water in transparent rhombic prisms, which dissolve in 0·75 part of cold, and 0·5 part of hot water, and have a strong but pleasant acid taste. Citric acid is also readily soluble in alcohol, and dissolves tolerably easily in ether. It melts at 100°, and on increasing the heat begins to lose its water of crystallization, which is driven off completely at about 130°. The anhydrous acid melts at 153°—154°, and decomposes at 175° into water and aconitic acid. On dry distillation citric acid decomposes into carbon dioxide, acetone, and two isomeric acids, itaconic and citraconic acids, $C_5H_6O_4$, which are likewise produced when citric acid is heated under pressure with water or with a dilute acid.

[1] *Compt. Rend.* xc. 1252.

When oxidized with manganese dioxide and dilute sulphuric acid, or with an acidified solution of potassium permanganate, carbon dioxide and acetone are formed.[1] If chlorine be led into an aqueous solution of citric acid exposed to sunlight, hexchloracetone is produced, whilst a solution of the sodium salt similarly treated yields pentachloracetone.[2] Bromine has no action upon a solution of the acid,[3] but when the sodium salt is thus treated, pentabromacetone is formed.[4] When citric acid is fused with caustic potash, two molecules of acetic acid are formed to one molecule of oxalic acid (Liebig):

$$C_6H_5K_3O_7 + KOH = 2C_2H_3KO_2 + C_2K_2O_4.$$

Citric acid when heated with syrupy phosphoric acid decomposes into water, carbon monoxide, carbon dioxide and acetone:

$$C_3H_5O(CO_2H)_3 = C_3H_6O + 2CO_2 + CO + H_2O.$$

Concentrated sulphuric acid produces a similar decomposition, but carbonization also occurs, and sulphur dioxide is evolved.[5]

Citric acid is used for domestic purposes and for the preparation of lemonade and other cooling drinks. It likewise finds employment in medicine, and in dyeing and calico-printing, where it is frequently replaced by the lemon-juice.

## The Citrates.

768 The salts of citric acid have been made the subject of careful examination by a number of chemists.[6]

*Normal Potassium Citrate*, $C_6H_5O_7K_3 + H_2O$, crystallizes in glassy needles, which have an alkaline taste, are deliquescent, and do not dissolve in absolute alcohol (Heldt).

*Monacid Potassium Citrate*, $C_6H_6O_7K_2$, dissolves readily in water, has a pleasant sour taste, and forms monoclinic crystals (Heusser).

*Diacid Potassium Citrate*, $C_6H_7O_7K + 2H_2O$, crystallizes in large transparent prisms, which have a sour taste and are permanent in the air.

[1] Péan de St. Gilles, *Compt. Rend.* xlvii. 554.
[2] Städeler, *Ann. Chem. Pharm.* cxi. 299.
[3] Cloëz, *ib.* cxxii. 116.
[4] Grimaux, *Compt. Rend.* lxxviii. 1442.
[5] Vangel, *Ber. Deutsch. Chem. Ges.* xiii. 355.
[6] Berzelius, *Pogg. Ann.* xxvii. 281; xlvii. 309; Liebig, *Ann. Pharm.* v. 134; xxvi. 151; xliv. 57; Heldt, *ib.* xlvii. 157; Kämmerer, *ib.* cxlviii. 294; clxx. 176; Heusser, *Pogg. Ann.* lxxxviii. 121; Landrin, *Compt. Rend.* lxxxvi. 1336.

The citrates of *sodium* and *ammonium* also dissolve easily and crystallize well.

*Normal Calcium Citrate*, $(C_6H_5O_7)_2Ca_3 + 4H_2O$. When a solution of normal sodium citrate is decomposed by the addition of calcium chloride solution, a thick white precipitate is quickly formed, which becomes crystalline by boiling. When one of the solutions is in excess, or if the liquids are very dilute, the precipitate is formed only on boiling. A solution of citric acid when treated with an excess of lime-water yields a precipitate only on heating, and this in part redissolves on cooling, as it is more soluble in cold than in hot water. According to Warrington, one part of the crystalline salt dissolves at 14° in 1180, and at 90° in 1730 parts of water.[1] The amorphous salt is more easily soluble, a fact already observed by Liebig.

Calcium citrate dissolves readily in acids, even in acetic acid. If ammonia be added to this solution, the salt separates out again slowly but completely in the cold (Warrington), whilst on heating the precipitate makes its appearance at once.

*Acid Calcium Citrate*, $C_6H_6O_7Ca + H_2O$, is obtained in glistening plates, when a solution of the normal salt in citric acid is evaporated. It is decomposed by water.

*Normal Barium Citrate*, $(C_6H_5O_7)_2Ba_3$. When baryta-water is added to a solution of citric acid, or barium chloride to a solution of a normal citrate, an amorphous precipitate is formed which is somewhat soluble in water and has the composition $(C_6H_5O_7)_2Ba_3 + 7H_2O$. The same salt is obtained when barium acetate is used; but when this is added in excess and the mixture heated in a covered vessel on the water-bath, the precipitate after some hours becomes dense and crystalline, and has then the formula $2(C_6H_5O_7)_2Ba_3 + 7H_2O$. This consists of microscopic glistening, clino-rhombic prisms, the form of which is so characteristic that this reaction serves for the detection of citric acid in fruit, juices, &c. The solution must not, however, be too dilute, as in this case it yields on heating the salt $(C_6H_5O_7)_2Ba_3 + 5H_2O$, which separates in needles.[2]

*Normal Magnesium Citrate*, $(C_6H_5O_7)_2Mg_3 + 14H_2O$, is obtained in crystalline crusts when a solution of citric acid not quite saturated with magnesia is evaporated at 50°. It is readily soluble in water, and has a much less unpleasant taste than Epsom salts,[3]

[1] *Journ. Chem. Soc.* 1875, 939.
[2] Kämmerer, *Frescnius' Zeitsch.* viii. 298.
[3] *Ann. Chim. Phys.* [5], xxv. 233.

and hence it is used as a mild purgative. A mixture of this salt with acid sodium carbonate, citric acid and sugar, which has been rendered granular by moistening with alcohol and redrying, forms the *Magnesia citrica effervescens* of the Pharmacopœia.

*Ferric Citrate*, $(C_6H_5O_7)_2Fe_2 + 6H_2O$, is obtained by dissolving freshly precipitated ferric hydroxide in citric acid, and gently evaporating the solution to the consistency of a syrup. It dries up to an amorphous mass usually consisting of thin hyacinth-red scales, is readily soluble in water, has a slight taste of iron, and is used in medicine. The similar hydrated double salt, $(C_6H_5O_7)_3Fe_2(NH_4)_3$, is also officinal.

When ferric hydroxide is dissolved in the right proportion in a solution of ammonium citrate, and this then evaporated, reddish brown crystals are obtained of the salt, $[C_6H_5O_7(NH_4)_2]_4Fe_2(OH)_2 + 4H_2O$. If, however, the ferric hydroxide be added in excess, amorphous scales are formed. Landrin has proposed the use of the crystalline salt for medicinal purposes, as the iron citrate of commerce contains a very variable quantity of iron. He has also prepared a series of double salts with other metals.[1]

*Silver Citrate*, $C_6H_5O_7Ag_3$, is a white precipitate which gradually becomes crystalline, and on boiling with water decomposes with separation of silver. When heated in a stream of hydrogen to 100°, it decomposes with separation of water into citric acid and *argentous citrate*, $2C_6H_5O_7(Ag_2)_3 + H_2O$, a brown powder, which dissolves slowly in water with a red colour, and is decomposed by potash solution with separation of silver tetrantoxide (Vol. II., Part I., 367).[2]

Silver citrate dissolves in boiling citric acid, and on cooling the acid salt, $C_6H_6O_7Ag_2$, crystallizes out in rhombic tablets.[3]

769 *Reactions of Citric Acid.* This acid is distinguished from tartaric acid by being optically inactive, and by not giving, on heating, the smell of burnt sugar, but yielding a vapour having a penetrating odour. Moreover, when lime-water is added in excess to its aqueous solution a precipitate is formed only when the solution is boiled, whilst tartaric acid produces a precipitate in the cold, and malonic acid gives no precipitate under these circumstances. Calcium citrate is insoluble in caustic alkalis whilst the tartrate readily dissolves (p. 225). The barium salt is also characteristic of citric acid (p. 434). When 1 part

[1] *Ann. Chim. Phys.* [5], xxv. 233.
[2] Wöhler, *Ann. Chem. Pharm.* xxx. 2.
[3] Rönnefahrt, *Jahresb.* 1876, 562.

of citric acid is heated with 6 parts of ammonia for six hours in a closed tube to 110°—120° and then poured into a shallow vessel and exposed to light, it becomes coloured blue in a few hours, and after some days this changes to green.[1] Citric acid is frequently adulterated with tartaric acid. In order to detect such an adulteration the concentrated solution is heated with potassium acetate, an equal volume of strong alcohol added, and the mixture well stirred, when, if tartaric acid is present, cream of tartar soon separates out.[2] If a quantitive determination be required, twice the volume of alcohol of 95 per cent. is added, the precipitate filtered off after an hour's standing, and this then washed with a mixture of water and twice its volume of alcohol. The filtrate is precipitated with lead acetate, and the precipitate after washing with 50 per cent. alcohol is decomposed by sulphuretted hydrogen. The citric acid can then be titrated with standard soda,[3] or it may be converted into the barium salt and this analysed.[4]

## Ethereal Salts of Citric Acid.

770 *Normal Methyl Citrate*, $C_6H_5O_7(CH_3)$, is obtained when hydrochloric acid is led into a solution of citric acid in methyl alcohol, the solution being warmed.[5] It forms triclinic crystals which melt at 78°·5—79°, and it boils at 270°—273° with partial decomposition into water and methyl aconitate. When heated with acetyl chloride, *methyl acetocitrate*, $C_3H_4(OC_2H_3O)(CO_2.CH_3)_3$, is obtained, a colourless liquid boiling at 280°—282°. When phosphorus pentachloride acts on methyl citrate, this is transformed into *methyl chlortricarballylate*, $C_3H_4Cl(CO_2CH_3)_3$, a thick, oily liquid, which on heating splits up into hydrochloric acid and methyl aconitate.[6]

*Dimethyl Citric Acid*, $C_6H_6O_7(CH_3)_2$, and *Methyl Citric Acid*, $C_6H_7O_7(CH_3)$, are also formed in the preparation of the normal salt, and are likewise produced by the action of citric acid on methyl alcohol, but as yet they have not been prepared pure. The calcium salt of the first is soluble in alcohol; whilst that of the second acid does not dissolve in this menstruum.[7]

[1] Sabanin and Laskowsky, *Fresenius' Zeitsch.* xvii. 74.
[2] Spiller, *Journ. Chem. Soc.* x. 110.
[3] Fleischer, *Fresenius' Zeitsch.* xiii. 328.
[4] Creuse, *Jahresb.* 1873, 970.
[5] St. Evre, *Compt. Rend.* xxi. 1441.
[6] Hunaeus, *Ber. Deutsch. Chem. Ges.* ix. 1749.
[7] Demondesir, *Compt. Rend.* xxxiii. 227.

*Normal Ethyl Citrate*, $C_6H_5O_7(C_2H_5)_3$, was obtained by Thénard[1] and Malaguti[2] by heating citric acid with alcohol and sulphuric acid. It is better prepared by saturating a solution of citric acid in alcohol with hydrochloric acid.[3] It is a thick odourless liquid, boiling at 283°, and possessing a very bitter taste. When treated with sodium amalgam and a little water, salts are produced of diethylcitric acid and ethylcitric acid (Claus). Heated with alcoholic ammonia in a closed vessel, a deep green or blue solution is obtained.[4]

*Ethyl Acetocitrate*, $C_3H_4(OC_2H_3O)(CO_2.C_2H_5)_3$, is obtained by the action of acetyl chloride on the normal salt, and is an oily liquid, which for the most part distils without change at 288°.[5]

*Tetraethyl Citrate*, $C_3H_4(OC_2H_5)(CO_2.C_2H_5)_3$, is obtained by the action of sodium and ethyl iodide on the normal salt. It is an oily liquid, having a pleasant smell and a slightly bitter taste. Under ordinary pressure it boils at 290° with considerable decomposition, but it boils without alteration at a reduced pressure.[6]

*Nitroxycitric Acid*, $C_3H_4(NO_3)(CO_2H)_3$, is formed when anhydrous citric acid is introduced into a mixture of 1 part of fuming nitric acid and two parts of sulphuric acid. It forms crystals which are readily soluble in water. On evaporating the solution, even in a vacuum, decomposition takes place.[7]

## Aconitic Acid, $C_6H_6O_6$.

771 This acid was discovered in 1820 by Peschier[8] in *Aconitum Napellus* and *A. paniculatum*, and was then further examined by Buckner[9] and Dahlström.[10] In 1828 Braconnot found in *Equisetum flaviale*, *E. hyemale*, etc. an acid to which the name of *equisetic acid* was given,[11] and this according to Regnault, who prepared the acid from *E. limosum*, is identical with maleic acid.[12]

[1] *Mem. Soc. d'Arcueil*, ii. 12. [2] *Ann. Chim. Phys.* lxiii. 197.
[3] Heldt, *Ann. Chem. Pharm.* xlvii. 195; Pebal, *ib.* xcviii. 67; Claus, *Ber. Deutsch. Chem. Ges.* viii. 867; Conen, *ib.* xii. 1653.
[4] Kämmerer, *Ber. Deutsch. Chem. Ges.* viii. 732.
[5] Wislicenus, *Ann. Chem. Pharm.* cxxix. 192.
[6] Conen, *Ber. Deutsch. Chem. Ges.* xii. 1654.
[7] Champion and Pellet, *Bull. Soc. Chim.* [2], xxiv. 448.
[8] Trommsdorff, *Neu Journ. Pharm.* v., 1, 93; viii. 1, 266.
[9] *Repert. Pharm.* lxiii. 145. [10] *Ann. Chim. Phys.* (3) xxx. 312.
[11] *Ann. Chim. Phys.* [2], xxxix. 5. [12] *Ib.* [2], lxii. 208.

Baup[1] then obtained *citridic acid* by heating citric acid, and this was considered by Berzelius to be identical also with aconitic acid, the correctness of this view being afterwards ascertained by Crasso.[2] The identity of equisetic acid and aconitic acid was afterwards established by Baup[3] and Dessaignes.[4]

Besides its occurrence in the above-named plants, aconitic acid is also found in *Delphinium consolida*,[5] *Adonis vernalis*,[6] *Achillea millefolia*,[7] in the beetroot,[8] in ordinary sugar-cane,[9] and in Sorghum sugar-cane.[10]

*Preparation.* Aconitic acid is best prepared from citric acid. For this purpose the acid is heated in quantities of 100 grams in small flasks until the exit tubes (which are about 0·5 m. long) are covered with oily drops. The fused contents of the flasks are then poured into a shallow basin, and 15 grams of water added for every 100 grams of acid taken. The basin is heated on the water-bath until the residue solidifies on cooling; this is then powdered and treated with ether free from water and alcohol, when most of the unaltered citric acid remains behind. Aconitic acid is obtained from the solution by evaporating off the ether, and it is then purified by recrystallization.[11] Another method is to pass hydrochloric acid for a day through citric acid heated to 140°, the product being then treated as above.[12]

*Properties.* Aconitic acid dissolves readily in water and is still more easily soluble in alcohol. It crystallizes in small four-sided plates, which melt at 186°—187° with decomposition (Behr). As already stated, it combines with hydrogen to form tricarballylic acid (p. 428), whilst with hypochlorous acid it yields *chlorcitric acid*, $C_3H_4Cl(OH)(CO_2H)_3$, a syrup which on heating with water, or more readily with milk of lime, is transformed into *oxycitric acid*, $C_3H_4(OH)_2(CO_2H)_3$; this latter is a viscous deliquescent mass, the calcium salt of which is a difficultly soluble crystalline powder (Pawolleck).

Aconitic acid is a strong tribasic acid. Its salts have been examined by Baup, Buchner, and Guinochet.[13] It is dis-

[1] *Ann. Chem. Pharm.* xix. 29; xxix. 169. [2] *Ib.* xxxiv. 56.
[3] *Ib.* lxxvii. 293. [4] *Compt. Rend.* xxx. 432.
[5] Wicke, *Ann. Chem. Pharm.* xc. 98.
[6] Linderos, *Ann. Chem. Pharm.* clxxxii. 365.
[7] Hlasiwetz, *Jahresb.* 1857, 331.
[8] Lippmann, *Ber. Deutsch. Chem. Ges.* xii. 1650.
[9] Behr, *ib.* x. 351. [10] *Ber. Deutsch. Chem. Ges.* xv. 1763.
[11] Pawolleck, *Ann. Chem. Pharm.* clxxviii. 153.
[12] Hunaeus, *Ber. Deutsch. Chem. Ges.* ix. 1751.
[13] *Compt. Rend.* xciv. 455.

tinguished from citric acid by its ready solubility in ether, and also in that on treating with an excess of lime-water and boiling it yields no precipitate; *calcium aconitate*, $(C_6H_3O_6)_2Ca_3 + 6H_2O$, forming small crystals soluble at 15° in 99 parts of water.

*Ethyl Aconitate*, $C_6H_3O_6(C_2H_5)_3$, is obtained by the action of hydrochloric acid on an alcoholic solution of the acid, and forms an oily liquid having an aromatic smell, and boiling at 275°.[1] This compound is also produced when normal ethyl citrate is heated with phosphorus trichloride,[2] this formation corresponding exactly to the conversion of the ethereal salt of a monobasic oxyacid into one of the acrylic acid series (p. 401).

## Pyrocitric Acids, $C_5H_6O_4$.

772 By the dry distillation of citric acid, Lassaigne in 1822 obtained a new acid which he termed *acide pyrocitrique*.[3] Baup then found that the distillate contains a second isomeric acid, and to this he gave the name of *acide citricique*, whilst he designated Lassaigne's acid (being the first discovered) as *acide citribique*, and to a third acid, contained in the residue, the name *acide citridique* (p. 438) was applied.[4]

The existence of Baup's volatile acid was questioned by Liebig,[5] but Crasso, who made this matter the subject of a new investigation, found that these three acids are in fact formed when citric acid is heated. He determined the conditions under which the formation of these acids takes place, and showed that the third acid is first formed, and that it is identical with aconitic acid. By the dry distillation of this he obtained Baup's new acid, for which he proposed the name *pyroaconitic acid*, or *itaconic acid*, which latter name is formed from that of aconitic acid by a transposition of its constituent letters. By heating this latter acid he obtained Lassaigne's acid, and this he termed *citraconic acid*.[6] This last, as Gottlieb has shown, is transformed by boiling with dilute nitric acid into a new isomeric acid, which he termed *mesaconic acid*.[7]

Each of these three acids on treatment with sodium amalgam yields pyrotartaric acid (p. 253), but when united with bromine

[1] Mercadante, *Journ. Prakt. Chem.* [2], iii. 356.
[2] Conen, *Ber. Deutsch. Chem. Ges.* xii. 1655.
[3] *Ann. Chim. Phys.* xxi. 100.
[4] *Ann. Chem. Pharm.* xix. 29; xxix. 169.
[5] *Ib.* xxvi. 120.
[6] *Ann. Chem. Pharm.* xxxiv. 53.
[7] *Ib.* lxxvii. 268.

they form three different dibrompyrotartaric acids.[1] With hydrobromic acid, on the other hand, the two last acids give one and the same monobrompyrotartaric acid, whilst itaconic acid yields one different from these.[2]

773 *Itaconic Acid.* When citric acid is heated it splits up, as has already been described, yielding water and aconitic acid. This latter acid on heating to 200°—220° gives a distillate which separates into two layers, the one heavy and oily and the other lighter and aqueous. When these are mixed, heat is evolved and a crystalline mass is formed, saturated with an oily liquid. The crystals consist of itaconic acid, whilst the oily liquid is citraconic anhydride.[3] Their formation is explained as follows. The aconitic acid decomposes in the first place (probably with a preliminary transformation into anhydride) into water, carbon dioxide, and the anhydride of itaconic acid:

$$C_6H_6O_6 = H_2O + CO_2 + C_5H_4O_3.$$

This last is transformed on distillation in part into citraconic anhydride, which combines with water but slowly in the cold, whilst itaconic anhydride is readily converted into the acid by contact with water. The distillate also contains a considerable quantity of acetone, which is formed from the citric acid according to the following equation:

$$\begin{array}{l} CH_2.CO_2H \\ | \\ C(OH).CO.OH \\ | \\ CH_2.CO_2H \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + H_2O + CO + 2CO_2.$$

Itaconic acid is also produced when aconitic acid is heated with water to 180°,[4] or when citric acid is heated to 160° with pure water or water acidulated with sulphuric acid.[5] It is, however, best obtained from citraconic anhydride, the preparation of which will be described later. The anhydride is heated in a closed tube with twice or thrice its volume of water for six to eight hours to a temperature of 150°, the itaconic acid is allowed to crystallize out from the solution placed for this purpose in

[1] Kekulé, *Ann. Chem. Pharm.* Suppl. i. 338; ii. 94.
[2] Fittig and Landolt, *Ann. Chem. Pharm.* clxxxviii. 71.
[3] Anschütz, *Ber. Deutsch. Chem. Ges.* xiii. 1541.
[4] Pebal, *Ann. Chem. Pharm.* xcviii. 94.
[5] Markownikow and Purgold, *Zeitsch. Chem.* 1867, 264.

shallow vessels, and when the mother-liquor will yield no more crystals, it is again treated with water as already described.[1]

Itaconic acid crystallizes in rhombic pyramids or tables, which melt at 161° and dissolve at 20° in 12 parts of water. It dissolves more easily in alcohol and is also soluble in ether. By electrolysis of its calcium salt it is decomposed into hydrogen, carbon dioxide, and iso-allylene, in addition to acrylic acid and mesaconic acid which also are formed.[2]

774 *Itaconic Andydride*, $C_5H_4O_3$, is obtained, as has already been stated, as a product of the distillation of citric acid, and it is also formed when itaconic acid is warmed with acetyl chloride. It crystallizes from glacial acetic acid in transparent prisms, which melt at 68°. Under a diminished pressure of 30 mm. it boils at 139°—140°, the boiling point of citraconic anhydride being lower than this. On distillation under ordinary pressure itaconic anhydride is transformed into the last-named compound.[3] That this decomposition is not completely effected in the distillation of citric acid is explained by the fact that by means of the carbon dioxide, which is evolved in large quantity, it is carried over before it attains the temperature necessary for its decomposition. This also explains the observation of Crasso, that the yield of itaconic acid is the larger according as the distillation of the citric acid is the more rapidly conducted and as the retort is the more protected from the heat.[4]

*Itachlorpyrotartaric Acid*, $C_5H_7ClO_4$, is formed by heating itaconic acid with fuming hydrochloric acid to 130°. It crystallizes from water in warty masses, which melt at 140°—145°, and on heating to 150° in a stream of dry air it is converted into the anhydride. When heated with water, hydrochloric acid is given off and the first product is *paraconic acid*, $C_5H_6O_4$, which is also obtained by the action of silver oxide, and is a crystalline mass melting at 70°, and yielding citraconic anhydride on distillation. Together with this, *itamalic acid*, $C_5H_7(OH)O_4$, an homologue of malic acid, is always formed The alkalis and alkaline-earths effect this change much more quickly, whilst ammonia splits up the chlorinated acid into hydrochloric and mesaconic acids.[5]

[1] Willm, *Ann. Chem. Pharm.* cxli. 28; Aarland, *Journ. Prakt. Chem.* [2], vi. 262; Fittig and Landolt, *Ann. Chem. Pharm.* clxxxviii. 71.
[2] Swarts, *Zeitsch. Chem.* 1866, 721.
[3] Anschütz and Petri, *Ber. Deutsch. Chem. Ges.* xiii. 1539.
[4] Anschütz, *Ber. Deutsch. Chem. Ges.* xiii. 1541.
[5] Swarts, *Zeitsch. Chem.* 1866, 721.

*Itabrompyrotartaric Acid*, $C_5H_7BrO_4$, is obtained by heating itaconic acid with hydrobromic acid (Swarts), or by allowing it to stand for some days in contact with hydrobromic acid saturated at 0°, and shaking the mixture from time to time.[1] It is readily soluble in water and forms small, monoclinic crystals, which melt at 137°. When heated for some hours with water, itamalic acid is formed, whilst at the same time a portion is reconverted into itaconic acid. The same products are quickly obtained when sodium carbonate or calcium carbonate is added.

*Itamalic Acid*, $C_5H_8O_5$, crystallizes in long very deliquescent needles, which melt at 64°, and on distillation it decomposes into water and itaconic acid or citraconic anhydride.[2]

*Chloritamalic Acid*, $C_5H_7ClO_5$, is obtained by acting with chlorine on a solution of itaconic acid [3] or of its sodium salt,[4] and forms glistening monoclinic crystals which dissolve readily in water.

775 *Itadibrompyrotartaric Acid*, $C_5H_6Br_2O_4$, is formed by the direct union of bromine and itaconic acid and crystallizes in crusts readily soluble in water.[5] When boiled with water and an excess of sodium carbonate, the sodium salt of *aconic acid*, $C_5H_4O_4$, is obtained, which crystallizes in thin plates. If this be then decomposed with dilute sulphuric acid and extracted with ether, the acid is obtained after evaporation of the ether in characteristic tufts of long plates having a satiny lustre. It separates from water in glistening rhombic crystals, which melt at 164°. It is a monobasic acid, but on boiling with baryta-water, the barium salt is obtained of the liquid dibasic acid *oxyitaconic acid*, $C_5H_6O_5$, a compound which has not been further examined. By the continued action of baryta-water the acid is split up into formic and succinic acids. Aconic acid is not attacked by acetic anhydride.[6] It does not combine with bromine at the ordinary temperature and it is decomposed when heated with bromine.[7] The constitution of this compound and of the others belonging to this group will be discussed hereafter.

*Itatartaric Acid*, $C_5H_6(OH)_2O_4$, is produced by acting with silver oxide on a solution of itadibrompyrotartaric acid,[8] or by

[1] Fittig and Landolt, *Ann. Chem. Pharm.* clxxxviii. 71.
[2] Swarts, *Zeitsch. Chem.* 1867, 648 ; Fittig and Landolt, *loc. cit.*
[3] Swarts, *Jahresb.* 1873, 583.
[4] Morawski, *Journ. Prakt. Chem.* [2], vii. 158.
[5] Kekulé, *Ann. Chem. Pharm.* Suppl. i. 339.
[6] Meilly, *Ann. Chem. Pharm.* clxxi. 153.
[7] Wichelhaus, *ib.* clxxi. 182.
[8] Kekulé, *Ann. Chem. Pharm.* Suppl. i. 343.

boiling chlor-itamalic acid with caustic lime.[1] It forms a glassy deliquescent mass, but many of its salts crystallize well. The calcium salt $2C_5H_6O_6Ca + H_2O$, is a difficultly soluble crystalline precipitate.

776 *Citraconic Acid*, $C_5H_6O_4$. To prepare this, about 100 grams of citric acid are subjected to dry distillation; from the distillate the citraconic anhydride formed is separated by repeated acid rectification, and this in contact with water gradually combines to form the acid.[2]

Citraconic acid forms monoclinic deliquescent prisms which dissolve at the ordinary temperature in less than half their weight of water. On distillation, the acid decomposes again into water and the anhydride, but it volatilizes with moderate ease in a current of steam whilst on heating with water to 120° it is transformed into itaconic acid. Its potassium salt yields on electrolysis allylene, together with but little acrylic and mesaconic acids (Aarland).

*Citraconic Anhydride*, $C_5H_4O_3$, is a colourless heavy liquid which boils at 213°—214°.

*Citrachlorpyrotartaric Acid*, $C_5H_7ClO_4$, separates out gradually when citraconic anhydride and fuming hydrochloric acid are allowed to stand together. It crystallizes from warm water in glistening tables or plates which melt at 129°.[3] When heated with sodium carbonate solution it decomposes into hydrochloric acid, carbon dioxide, and methacrylic acid, $C_4H_6O_2$ (p. 406).

*Citrabrompyrotartaric Acid*, $C_5H_7BrO_4$, is formed by the union of the acid or its anhydride in the cold with fuming hydrobromic acid, and forms transparent well-formed crystals belonging to the monoclinic system, which melt at 148° (Fittig and Landolt). When boiled with a solution of carbonate of soda it yields methacrylic acid, and when its silver salt is heated with water to 130° it splits up into carbon dioxide, silver bromide, and allylene.[4]

*Citramalic Acid*, $C_5H_7(OH)O_4$, is obtained by the action of zinc on an aqueous solution of chlorcitramalic acid,[5] and forms large crystals which melt at 119°, and on distillation split up into water and citraconic anhydride.[6]

[1] Morawski, *Journ. Prakt. Chem.* [2], xi. 450.
[2] Fittig and Landolt, *Ann. Chem. Pharm.* clxxxviii. 71.
[3] Swarts, *Zeitsch. Chem.* 1866, 724; Fittig and Landolt, *Ann. Chem. Pharm.* clxxxviii. 83.
[4] Bourgoin, *Bull. Soc. Chim.* xxviii. 459.
[5] Carius, *Ann. Chem. Pharm.* cxxix. 160
[6] Morawski, *Jahresb.* 1878, 721.

*Chlorcitramalic Acid*, $C_5H_6Cl(OH)O_4$, is produced by acting with hypochlorous acid on a citraconate,[1] or by leading chlorine into a solution of citraconic acid or its sodium salt.[2] Mesaconic acid also is transformed in this way into chlorcitramalic acid.[3] It dissolves readily in water and forms glistening crystals which melt at about 100°. When boiled with an excess of baryta-water it is transformed into *oxycitraconic acid*, $C_5H_5(OH)O_4$, which crystallizes in fine prisms and unites with hydrochloric acid at 100° to form *isochlorcitramalic acid*. This forms tables which melt at 160°, and is probably *chlormesamalic acid*.

*Citratartaric Acid*, $C_5H_4(OH)_2O_4$, was obtained by Carius by mixing barium chlorcitramalate with baryta-water, evaporating at 100,° and decomposing the residue with sulphuric acid. It is also formed when 1 part of chlorcitramalic acid is heated with 10 parts of water to 100° for twelve hours (Morawski). On evaporation it remains as a syrup which gradually becomes crystalline.

*Citradibrompyrotartaric Acid*, $C_5H_6Br_2O_4$. Bromine unites readily with citraconic acid in the cold forming this acid, which forms fine crystals that melt at 150° and dissolve easily in water. When boiled with water, or with sodium carbonate solution, it splits up into carbon dioxide, hydrobromic acid, brommethacrylic acid, and propionaldehyde.[4]

777 *Mesaconic Acid*, $C_5H_6O_4$, was obtained by Gottlieb by warming citraconic acid with dilute nitric acid, and he also pointed out that it cannot be obtained by a similar treatment of itaconic acid.[5] Its salts were then examined by Pebal.[6] Baup also examined this acid and termed it *acide citracartique* (from *acide citraconique* and *ars*).[7]

It is also produced when citraconic acid is warmed with hydriodic acid (Kekulé), hydrochloric acid (Swarts), or hydrobromic acid (Fittig); or when the acid or itaconic acid is heated with water to 180°—200°.[8] For its preparation a mixture of 2 parts of citraconic anhydride, 2 parts of water, and 3 parts of nitric acid of sp. gr. 1·074 is evaporated until

[1] Carius, *Ann. Chem. Pharm.* cxxvi. 201; cxxix. 164.
[2] Gottlieb, *ib.* clx. 101.
[3] Morawski, *Journ. Prakt. Chem.* [2], x. 79; xi. 466.
[4] Fittig and Krusemark, *Ann. Chem. Pharm.* ccvi. 1.
[5] *Ann. Chem. Pharm.* lxxvii. 268.
[6] *Ib.* lxxviii. 129.
[7] *Ann. Chim. Phys.* [3], xxxiii. 192.
[8] Swarts, *Jahresb.* 1873, 579.

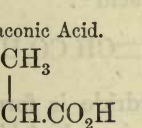
red fumes are evolved, and the acid which separates out on cooling is re-crystallized from hot water (Fittig and Landolt).

Mesaconic acid crystallizes from water in fine needles and from alcohol in transparent prisms; it melts at 200°, and at a higher temperature volatilizes, without forming an anhydride, and yields a vapour having an irritating odour. One hundred parts of water dissolve 2·7 parts of the acid at 18°, and 117·9 parts at the boiling point (Pebal). Its potassium salt yields on electrolysis the same products as are obtained when potassium citraconate is similarly treated (Aarland). The acid unites with fuming hydrochloric or hydrobromic acid when heated, producing the corresponding derivatives of citraconic acid (Fittig and Landolt).

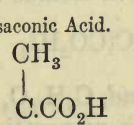
*Mesadibrompyrotartaric Acid*, $C_5H_6Br_2O_4$, is formed by the direct union of bromine with mesaconic acid, heat being required to effect the combination. It forms warty crystals and is less soluble in water than citradibrompyrotartaric acid (Kekulé, Fittig, and Landolt). When boiled with water it decomposes into hydrobromic acid and the anhydride of bromcitraconic acid, whilst at the same time some propionaldehyde is also produced. If, however, it be boiled with a solution of sodium carbonate, it yields the same products as citradibrompyrotartaric acid does, together with isobrommethacrylic acid (Fittig and Krusemark).

778 *The Constitution of the Pyrocitric Acids.* When the properties of citraconic and mesaconic acids, are compared with one another, it is evident that these bodies stand in the same relation to one another as fumaric and maleic acids do; differing from these latter by containing a methyl group in the place of an atom of hydrogen. Their isomerism therefore may be explained by a difference in the arrangement of their atoms in the molecule (p. 214), or the supposition of Fittig may be adopted, that as citraconic acid forms additive products readily in the cold, it contains free combining units, whilst in mesaconic acid these do not exist, thus leading to the following formulæ:

Citraconic Acid.



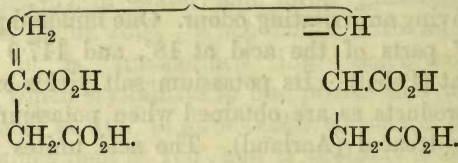
Mesaconic Acid.



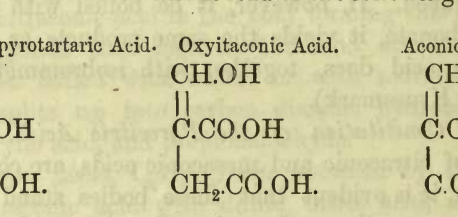
Itaconic acid is distinguished from these inasmuch as on

decomposition it yields isoallylene but no allylene, and consequently does not contain a methyl group. Its constitution will therefore be represented by one of the following formulæ:

Itaconic Acid.



Of these, Fittig considers the latter to be the more probable formula, as itaconic acid forms additive products as readily as does citraconic acid. It also explains in a simple manner the formation of monobasic aconic acid from itadibrompyrotartaric acid, whilst its properties of not combining with bromine in the cold and being unattacked by acetyl chloride shows that it contains no alcoholic hydroxyl. Baryta-water converts it into dibasic oxyaconic acid, which readily decomposes into formic and succinic acids. These observations lead to the following formulæ:[1]



779 *Crotaconic Acid,* $C_3H_4(CO_2H)_2$. This acid, isomeric with pyrocitronic acid, is prepared from β-chlorcrotonic acid. The ethyl salt of this is heated with potassium cyanide and alcohol, when *potassium β-cyancrotonate,* $CH_3.CH{=}C(CN)CO_2K$, is obtained, which forms small hard crystals and is transformed by hydrochloric acid into crotaconic acid. This latter exists in ill-defined, readily soluble crystals, which melt at 119° and decompose above 130° into carbon dioxide and crotonic acid[2]:

$$CH_3.CH{=}C(CO_2H)_2 = CH_3.CH{=}CH.CO_2H + CO_2.$$

*Xeronic Acid,* $C_8H_{12}O_4$. The anhydride is formed as a by-product in the preparation of citraconic anhydride, and is also obtained in smaller quantity on distilling this substance, also,

[1] *Ann. Chem. Pharm.* clxxxviii. 100.
[2] Claus and Wasowicz, *Ann. Chem. Pharm.* cxci. 33.

and in large amount, together with other bodies, when it is boiled some time:

$$2C_5H_4O_3 + H_2O = C_8H_{10}O_3 + 2CO_2.$$

It is a peculiarly smelling liquid, but little soluble in water, possessing at first a sweet but afterwards a bitter taste, and boiling at 242°. When dissolved in ammonia, and calcium chloride added, a crystalline precipitate is formed of *calcium xeronate*, $C_8H_{10}O_4Ca + H_2O$, and this when treated with hydrochloric acid does not yield xeronic acid, but is transformed again into the anhydride. It is from this behaviour that the acid derives its name (ξηρός, dry, anhydrous).

The empirical formula of xeronic acid shows that it is homologous with citraconic acid, but it possesses properties very different from this, inasmuch as it does not combine either with nascent hydrogen or with bromine.

On oxidation with solution of chromic acid it yields propionic acid. It must therefore be regarded as di-ethylfumaric acid.[1]

*Suberocarboxylic Acid*, or *Hexenyl Tricarboxylic Acid*, $C_6H_{11}(CO_2H)_3$. By passing chlorine into fused suberic acid, *monochlorsuberic acid*, $C_6H_{11}Cl(CO_2H)_2$, is produced as a syrupy liquid readily soluble in water and in ether. This is transformed into the above acid when heated with potassium cyanide solution and then boiled with potash. It forms fine glistening crystals.[2]

[1] Roser, *Ber. Deutsch. Chem. Ges.* xv. 2012.
[2] Bauer and Gröger, *Monatsch. Chem.* i. 510.

## HYDROCARBONS OF THE ACETYLENE SERIES $C_nH_{2n-2}$.

780 A general method for the preparation of this series of hydrocarbons consists in heating the haloid ethereal salts of the dyad alcohol radicals with alcoholic potash, when the reaction takes place in two stages:

Ethylene Bromide. Bromethylene.

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + KOH = \begin{array}{l} CH_2 \\ \| \\ CHBr. \end{array} + KBr + H_2O.$$

Acetylene.

$$\begin{array}{l} CH_2 \\ \| \\ CHBr \end{array} + KOH = \begin{array}{l} CH \\ \|\| \\ CH \end{array} + KBr + H_2O.$$

These hydrocarbons may be arranged in three classes:[1]

(1) Those of the first class are the true homologues of acetylene, and contain, like it, carbon atoms trebly linked. They are obtained from the dibromides of those olefines whose constitution admits of a treble linkage of the carbon atoms:

Methylacetylene.

$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_2Br \end{array} = \begin{array}{l} CH_3 \\ | \\ C \\ \|\| \\ CH \end{array} + 2HBr.$$

Methyl-ethyl-acetylene.

$$CH_3.CHBr.CHBr.C_2H_5 = CH_3.C{\equiv}C.C_2H_5 + 2HBr.$$

They are also obtained from the dichlorides formed by the action of phosphorus pentachloride on the aldehydes; heptaldehyde, $C_6H_{13}COH$, thus yields *pentylacetylene*, $C_5H_{11}C{\equiv}CH$. In

[1] Henry, *Ber. Deutsch. Chem. Ges.* viii. 400.

the same way they are produced from certain ketones; thus methyl-ethyl-ketone yields *ethyl acetylene*:

$$C_2H_5.CO.CH_3 = C_2H_5.C{\equiv}CH + H_2O.$$

The hydrocarbons of this class may also be obtained from acetylene, by the replacement of one or both atoms of hydrogen by alcohol radicals.

The two hydrogen atoms of acetylene may readily be replaced by certain metals, such as silver and copper, and its homologues which contain the group, —C≡CH, possess one hydrogen atom which admits of similar replacement. These may, therefore, be recognised by the fact that in ammoniacal solution they yield a precipitate with a silver salt or with cuprous chloride, whilst the hydrocarbons containing two alcohol radicals do not do so.

(2) The hydrocarbons of the second class contain the group —HC=C=CH—, and are derived from the haloid ethereal salts of olefines, or from those obtained from ketones, in which a treble linkage of the carbon atoms cannot occur. Thus amylene bromide yields *dimethyl-isoallylene:*

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CBr.CHBr.CH_3 = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}C{=}CH_2 + 2HBr.$$

And the chloride obtained from di-isopropyl ketone yields *tetramethyl-allylene:*

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH.CCl_2.CH\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix} = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}C{=}C\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix} + 2HCl.$$

These hydrocarbons do not yield any metallic compounds.

(3) The members of the third class contain two groups of doubly-linked carbon atoms. The only member of the class yet known is *diallyl*, $C_6H_{10}$, obtained by the action of sodium on allyl iodide, and having the constitution $CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$. This also does not contain any hydrogen atom replaceable by metals.

The hydrocarbons of the $C_n\,C_{2n-2}$ series are also produced by the electrolysis of acids of the series $C_n\,H_{2n-4}O_4$; thus fumaric acid yields acetylene:

$$\begin{matrix} CH.CO_2H \\ \| \\ CH.CO_2H \end{matrix} = \begin{matrix} CH \\ \| \\ CH \end{matrix} + 2CO_2 + H_2;$$

whilst itaconic acid gives *isoallylene*:

$$\begin{array}{l} CH_2 \\ \| \\ C.CO_2H \\ | \\ CH_2.CO_2H \end{array} = \begin{array}{l} CH_2 \\ \| \\ C \\ \| \\ CH_2 \end{array} + 2CO_2 + H_2.$$

They are also found amongst the products of the dry distillation of various organic substances.

These hydrocarbons unite with the elements of the chlorine group to form two classes of compounds, the first class being formed by the addition of two atoms of the chlorous element. The bodies thus obtained belong to the olefine type, and they again combine with two more atoms of the halogen. They behave similarly with the hydracids, the halogen combining with the carbon atom poorest in hydrogen.

## ETHINE COMPOUNDS.

781 *Acetylene*, or *Ethine*, $C_2H_2$, was first examined by Edmund Davy, who obtained it by the action of water on the greyish-brown mass produced by heating carbonized tartar and charcoal powder together in an attempt to prepare potassium. He described the gas as a new hydrocarbon which he called klumene, but did not submit it to further examination, the mass from which it was obtained being considered by him to be a carburet of potassium.[1]

These observations were however quite forgotten until Berthelot re-discovered this hydrocarbon and gave to it the name of acetylene.[2] He obtained it by passing ethylene, or the vapours of wood-spirit, alcohol, ether, &c., through a red-hot tube. Berthelot also observed its existence in coal-gas, which, however, contains only about 0·06 per cent. He found further, that it is produced when an induction-spark is passed through marsh gas, ethylene, or a mixture of cyanogen and hydrogen, and also when the vapours of ether, amylene, and other volatile carbon compounds undergo incomplete combustion.

*Synthesis.* By far the most important observation made by Berthelot on this subject is, however, the synthesis of acetylene

[1] *Ann. Chem. Pharm.* xxiii. 144.

[2] *Ann. Chim. Phys.* [3], lxvii. 52; [4], ix. 413; xiii. 143; *Brit. Assoc. Rep.* 1836 (part 2), pp. 62—64; Thomson, *Records*, iv. 1836, pp. 321—323.

which he effected by passing a powerful electric current between two carbon poles in an atmosphere of hydrogen. The apparatus which he employed is shown in Fig. 119. The glass vessel O is closed by doubly-bored corks which carry glass tubes, the narrow tubes (t t) serving for conducting hydrogen to and from the vessel, whilst through the wider tubes (T T) stout copper rods pass. One end of each of these is attached to poles of purified gas-carbon, the other end being connected with a battery of 50 Bunsen elements. The acetylene formed by the action of the electric arc, mixed with hydrogen, is passed into an ammoniacal solution of cuprous chloride, and the red insoluble copper compound thus obtained (which is more fully described further on), is then treated with hydrochloric acid, when acetylene is liberated.[1]

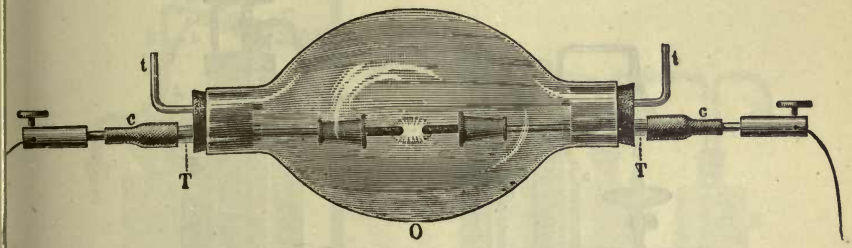



Fig. 119.

Another interesting fact respecting the formation and decomposition of acetylene has been recently noted by Berthelot.

In the combination of carbon and hydrogen 61,100 units of heat are absorbed, so that the sudden decomposition of acetylene should cause a rise of temperature amounting to 3000°. But this sudden decomposition cannot be effected either by heat or by means of the electric spark; it can, however, easily be brought about by exploding by the spark 0·1 grm. of fulminating mercury in a volume of about 20 to 25 cbc. of acetylene, when a violent detonation occurs and the acetylene is suddenly decomposed into finely divided carbon and its own volume of hydrogen.[2]

Acetylene is likewise produced when the vapour of chloroform is passed over red-hot copper (Berthelot), or when chloroform is

[1] *Ann. Chim. Phys.* [3], lxvii. 52.
[2] Berthelot, *Bull. Soc. Chim.* xxxviii. 5.

heated with sodium.[1] It is formed also in the electrolysis of fumaric and maleic acids.[2]

782 *Preparation.* For its preparation ethylene bromide is allowed to drop slowly into a concentrated boiling solution of caustic potash in alcohol, the evolved gas being passed through a second similar boiling solution in order to free it from bromethylene.[3] According to Zeisel, the above treatment does not completely remove the latter compound, but this may be effected by passing the gas over moderately-heated soda-lime.[4]

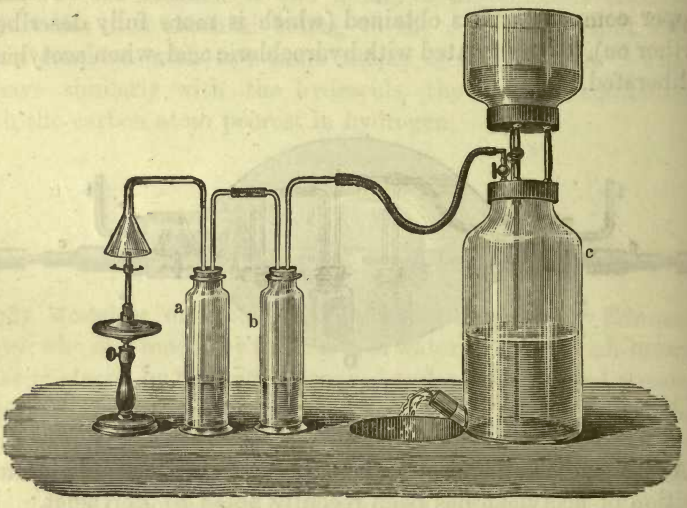



FIG. 120.

Acetylene is moreover formed in large quantity when the vapour of ethylene chloride is passed over heated lime or soda-lime.[5] It is also produced abundantly in the incomplete combustion of coal-gas, as may be well shown when the flame of a Bunsen-burner "burns down."[6] If a large glass globe be held for a few minutes over the burner and then a few drops of cuprous chloride poured over the inner surface of the globe a dark red film is formed on the sides of the vessel. To prepare the copper

[1] Fittig, *Zeitsch. Chem.* 1866, 127. [2] *Ann. Chem. Pharm.* cxxxi. 85.
[3] Miasnikow, *Ann. Chem. Pharm.* cxviii. 330; Sawitsch, *ib.* cxix. 184; Sabanejew, *ib.* clxxviii. 111. [4] *Ib.* cxci. 372.
[5] von Wilde, *Ber. Deutsch. Chem. Ges.* vii. 352.
[6] Rieth, *Zeitsch. Chem.* 1867, 598.

compound in larger quantity, the apparatus shown in Fig. 120 is employed, the products of combustion being drawn by means of an aspirator through a cylinder containing the ammoniacal copper solution. Since, however, a current of air accompanies the acetylene the cuprous oxide soon becomes oxidized and the formation of the red compound ceases. A richer yield of this latter compound is obtained when an apparatus is used similar to that described by Berthelot.[1] The burner, A A (Fig. 121), is connected with the brass tube, B B B, the downward bent portion of which is cooled in order to condense the water. This collects in F, whilst the gas is drawn through the cuprous solution by means of the aspiration of the Bunsen-pump. The stop-cock, U, serves

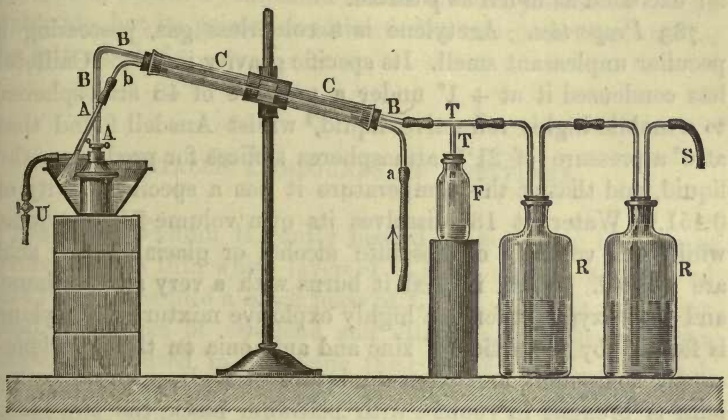



Fig. 121.

to regulate the stream of gas, so that neither coal-gas nor air is in excess. This apparatus may be kept at work for many days; every morning the current of gas is stopped for a quarter of an hour in order to allow the copper compound to settle. When sufficient quantity of the precipitate has been deposited in R, the flask is removed and replaced by a fresh one, and this in its turn by another flask containing the cuprous solution. The liquid is drawn off by means of a siphon, and the residue is washed repeatedly with distilled water until the ammonia is completely removed, as otherwise the moist compound quickly oxidizes. By treatment with hydrochloric acid ethylene is liberated, but

[1] *Ann. Chim. Phys.* [5], x. 365.

this always contains a little chlorethylene (Berthelot, Zeisel). By means of this apparatus Berthelot obtained in one night a quantity of the cuprous compound sufficient to yield four liters of acetylene. An improved form of the apparatus has been described by Jungfleisch.[1]

Berthelot gives the following process for the preparation of a solution best adapted for the absorption of acetylene. Cupric oxide is dissolved in cold commercial hydrochloric acid, and the solution is poured into flasks half filled with copper turnings. The liquid quickly becomes colourless and then commercial ammonia (well cooled by water) is added until the solution has a slightly acid reaction, after which the liquid is made alkaline with ammonia. All these operations must be quickly performed, and air excluded as much as possible.

783 *Properties.* Acetylene is a colourless gas, possessing a peculiar unpleasant smell. Its specific gravity is 0·91. Cailletet has condensed it at + 1° under a pressure of 48 atmospheres, to a mobile highly refractive liquid,[2] whilst Ansdell found that at 0° a pressure of 21·5 atmospheres suffices for producing the liquid, and that at this temperature it has a specific gravity of 0·451.[3] Water at 18° dissolves its own volume of acetylene, whilst six volumes of absolute alcohol or glacial acetic acid are needed. When ignited it burns with a very smoky flame, and with oxygen it forms a highly explosive mixture. Ethylene is formed by the action of zinc and ammonia on the acetylene-copper compound, and when a mixture of hydrogen and acetylene is brought in contact with platinum black, the two gases unite, forming ethylene.[4]

Acetylene unites with haloid hydracids, first forming mono-substitution-products of ethylene, and these combine with a second molecule of the acid, thus giving rise to ethidene compounds.[5]

Concentrated sulphuric acid slowly absorbs acetylene, and when this solution is diluted with water and distilled, croton-aldehyde (p. 403) passes over, the formation of which may be readily explained; acetylene combining with water first to form acetaldehyde, and this then condensing to crotonaldehyde.

[1] *Compt. Rend.* xc. 364.
[2] *Compt. Rend.* lxxxv. 851.
[3] *Chem. News*, xl. 136.
[4] von Wilde, *Ber. Deutsch. Chem. Ges.* vii. 353.
[5] Berthelot, *Ann. Chem. Pharm.* cxxxii. 122; Reboul, *Ber. Deutsch. Chem. Ges.* v. 326.

Chromic acid solution oxidizes acetylene to acetic acid, aldehyde being an intermediate product, whilst an alkaline solution of potassium permanganate transforms it into oxalic acid.

When acetylene is brought in contact with mercuric bromide and water, it combines with the latter slowly in the cold, or more quickly on heating, forming acetaldehyde. The part played by the mercuric bromide in this reaction is not understood. With water alone, or in the presence of hydrobromic acid, no combination occurs.[1]

Although acetylene is formed from its elements at the temperature of the electric arc, it is decomposed again by the passage of the induction spark (Berthelot).

Acetylene is poisonous, combining with the hæmoglobin of the blood to form a compound similar to that yielded by carbon monoxide, but its poisonous action is less energetic than that of the latter body.[2]

## Metallic Compounds of Acetylene.

784 When sodium is gently heated in acetylene it becomes covered with a thin white layer of $C_2HNa$, and at a dark red heat this passes into a black mass of $C_2Na_2$. At the same time small quantities of ethylene and ethane are formed. When potassium is fused in acetylene the compound $C_2K_2$ is formed, and the mass becomes incandescent. All these compounds are acted upon by water with explosive violence, acetylene being again formed.[3]

*Calcium Acetylide*, $C_2Ca$, is obtained when an alloy of calcium and zinc is strongly heated with charcoal. It is decomposed by water into calcium hydroxide and acetylene.[4]

*Cuprous Acetylide*, $C_2Cu_2 + H_2O$. Quet observed that when the induction spark is passed into alcohol, or when its vapour is passed through a red-hot porcelain tube, a gas is formed which yields precipitates with ammoniacal cuprous chloride solution and silver solution, and that these products explode when heated or on percussion.[5] Böttger obtained similar precipitates

[1] Kutscharow, *Ber. Deutsch. Chem. Ges.* xiv. 1540.
[2] Bistrow and Liebreich, *Ber. Deutsch. Chem. Ges.* i. 220.
[3] Berthelot, *Bull. Soc. Chim.* 1866, v. 182; *Ann. Chem. Pharm.* cxxxix. 150.
[4] Wöhler, *Ann. Chem. Pharm.* cxxiv. 220.
[5] *Comptes Rendus*, xlvi. 903; *Ann. Chem. Pharm.* cviii. 116.

by passing coal-gas through these solutions, and he termed the red flocculent substance a copper-hydrocarbon compound, as it is converted by hydrochloric acid into a gaseous hydrocarbon and cuprous chloride.[1] Torrey then stated that as early as 1839 he had found in the copper gas-pipes in New York a brown scaly deposit which exploded violently on percussion or when heated to 200°.[2] Berthelot was the first to examine this substance more minutely, and Crova pointed out that it is also formed when moist acetylene is brought into contact with metallic copper.[3]

The preparation of this copper compound has already been fully described. It forms a dark red amorphous precipitate, which when dry explodes either on percussion or on heating to about 100°—120°, leaving behind a velvety black powder which contains charcoal and copper. When brought in contact with chlorine, bromine, or finely divided iodine, ignition takes place. The formation of this compound is so characteristic and delicate that according to Berthelot the presence of 0·005 mg. of acetylene can thus be recognised.

The constitution of this compound has as yet not been ascertained. Berthelot gave to it the formula $(C_2HCu_2)_2O$, and termed it *cuproso-acetyl oxide*,[4] but Blochmann, on the other hand, found, as the result of very careful analysis, numbers giving the composition $C_2H_2Cu_2O$, which corresponds with the formula given above.[5] When acetylene is passed into a solution of cuprous chloride in potassium chloride a red precipitate is likewise produced, and this, according to Berthelot, is *cuproso-acetyl chloride*, $C_2HCu_2Cl$. If this formula be correct, the compound precipitated from ammoniacal solution will be the corresponding hydroxide, and the constitution of these compounds would be represented by the following formulæ:

| Cuproso-acetyl Hydroxide. | Cuproso-acetyl Chloride. |
|---|---|
| $CH{\equiv}C—Cu—Cu—OH.$ | $CH{\equiv}C—Cu—Cu—Cl.$ |

Berthelot has also prepared other cuproso-acetyl salts, but has not published any analyses.

*Silver Acetylide*, $C_2Ag_2 + H_2O$, is formed as a white or yellowish precipitate by passing acetylene into an ammoniacal

[1] *Ann. Chem. Pharm.* cix. 351.
[2] *Jahresb.* 1859, 222.
[3] *Ib.* 1862, 442.
[4] *Ann. Chem. Pharm.* cxxxviii. 245.
[5] *Ib.* clxxiii. 174.

solution of silver nitrate. In the dry state it explodes even more easily than the copper compound. Blochmann's analyses give the above formula, but Berthelot considers the compound to be *argentacetyl oxide*, $(C_2HAg_2)_2O$, and he has prepared the corresponding chloride, $C_2HAg_2Cl$, from a solution of silver chloride in ammonia.

If silver-acetylide be shaken up with a solution of iodine in ether until this is decolorized, and the liquid be then evaporated, yellow crystals are formed which have a repulsive odour, and the vapour strongly attacks the eyes. According to Berend they possess the formula $C_4H_2I_4$, and yield a large quantity of acetylene when heated with alcoholic potash.[1] The constitution of this compound is not known.

When acetylene is passed into an ammoniacal solution of aurous thiosulphate, a yellow highly explosive precipitate is formed, whilst in an alkaline solution of mercury potassium iodide a yellow precipitate is obtained having the composition $C_2HHgI,HgO$; this explodes slightly on heating, and yields acetylene on treatment with acids.[2]

## Haloid Ethereal Salts of Acetylene.

785 *Acetylene Dichloride*, $C_2H_2Cl_2$. When acetylene and chlorine are brought in contact deflagration usually occurs and carbon is separated. Sometimes, however, under conditions which have not as yet been determined, the dichloride is produced. This latter may be easily obtained pure by passing acetylene into moderately cooled antimony pentachloride, when crystalline plates of $C_2H_2Cl_2.SbCl_3$ are formed, and this on heating splits up into antimony trichloride and acetylene dichloride.[3] This latter is a mobile liquid, which boils at 55° and has an odour resembling that of chloroform.

*Acetylene Tetrachloride*, $C_2H_2Cl_4$, is obtained when the double compound just described is heated with an excess of antimony pentachloride, and also when phosphorus pentachloride acts on dichloracetaldehyde,[4] or when chlorine is passed into ethylene

[1] *Ann. Chem. Pharm.* cxxxv. 257.
[2] Basset, *Chem. News*, xix. 28.
[3] Berthelot and Jungfleisch, *Ann. Chem. Pharm.* Suppl. vii. 252.
[4] Paterno and Pisati, *Jahresb.* 1871, 508.

chloride (p. 41). It is a liquid boiling at 147°, and at 0° has a specific gravity of 1·614.

*Acetylene Dibromide*, $C_2H_2Br_2$, is produced by the union of acetylene and bromine,[1] but is not easily obtained pure in this way. It may, however, be readily prepared from the tetrabromide by decomposing its well-cooled alcoholic solution with zinc, and after the reaction is over, precipitating with water.[2] It is liquid having a chloroform-like smell, boiling at 110°—111°, and having at 23° a specific gravity of 2·20.

*Acetylene Tetrabromide*, $C_2H_2Br_4$, is obtained by passing acetylene into bromine under water. It is a liquid which at 17°·5 has a specific gravity of 2·9493. At 190° it decomposes into hydrobromic acid and tribromethylene, but under a pressure of 36 mm. of mercury it boils at 137°.[3]

*Acetylene Di-iodide*, $C_2H_2I_2$. This compound separates out in crystals when acetylene is passed into a mixture of iodine and absolute alcohol. The liquid is removed by the filter-pump, the residue washed with dilute potash solution and then recrystallized from hot alcohol. It forms long thin flexible needles which possess a strong and characteristic odour. It melts at 73°, but it volatilizes at the ordinary temperature, and may be sublimed without decomposition.

Together with this compound, an isomeric liquid di-iodide is formed which decomposes on heating, and also a more volatile iodine compound which escapes with the unabsorbed acetylene.[4]

## Substitution-products of Acetylene.

786 *Monochloracetylene*, $C_2HCl$. By the reduction of chloraldid (Part I. p. 538) a dichloracrylic acid is produced, and this on boiling with baryta-water decomposes into monochloracetylene, hydrochloric acid, and carbon dioxide:

$$CCl_2{=}CH.CO_2H \;=\; CCl{\equiv}CH \;+\; HCl \;+\; CO_2.$$

The pure gas is spontaneously explosive, yielding carbon and hydrochloric acid, but does not explode when it is diluted with hydrogen. When this mixture is passed into bromine it forms the

[1] Berthelot, *Ann. Chem. Pharm.* cxxiv. 272; Sabanejew, clxxviii. 116.
[2] Sabanejew, *Ber. Deutsch. Chem. Ges.* ix. 1441; Anschutz, *ib.* xii. 2074.
[3] Sabanejew, *Ann. Chem. Pharm.* clxxviii. 113.
[4] *Ibid.* clxxviii. 118.

crystalline tetrabromide $C_2HClBr_4$, a substance which is also produced when bromine acts upon ethyl chloride, and is known as *a-chlortetrabromethane*.[1]

When passed into a solution of cuprous chloride in ammonia, monochloracetylene produces a yellowish red precipitate, whilst with silver nitrate solution a white precipitate is formed. Both compounds are highly explosive.[2]

*Monobromacetylene*, $C_2HBr$, is formed when bromethylene dibromide is heated with alcoholic potash.[3] The gas thus produced is mixed with much free acetylene. An almost pure product is got by the decomposition of dibromethylene dibromide according to the following equation:

$$CH_2Br—CBr_3 = CH{\equiv}CBr + HBr + Br_2.$$

The bromine which is liberated oxidizes the alcohol to formic acid.[4]

The gas liquefies under a pressure of three atmospheres, and in the air it takes fire and burns with a purple-coloured, very smoky flame. When brought in contact with oxygen explosion occurs. If, however, the compound be diluted with an indifferent gas and the mixture brought in contact with air, white clouds of bromacetic acid are produced.[5] With an ammoniacal solution of cuprous chloride it produces a red precipitate, which, according to Reboul, is copper acetylide. It unites with bromine, forming pentabromethane.

## PROPINE COMPOUNDS.

787 *Methyl-Acctylene*, or *Allylene*, $CH_3.C{\equiv}CH$, was first obtained by Markownikow by heating propylene bromide with alcoholic potash,[6] and almost simultaneously by Sawitsch by acting on brom-propylene with a solution of sodium ethylate.[7] It is also formed by heating $\beta$-chlorpropylene with caustic potash and alcohol,[8] and further, by the action of sodium on dichlorinated

[1] Denzel, *Ber. Deutsch. Chem. Ges.* xi. 1739.
[2] Wallach, *Ann. Chem. Pharm.* cciii. 87.
[3] Sawitsch, *Ann. Chem. Pharm.* cxix. 183 ; Reboul, *ib.* cxxiv. 267.
[4] Reboul, *ib.* cxxv. 81.
[5] Fontaine, *ib.* clvi. 269.
[6] *Ann. Chem. Pharm.* cxviii. 330. [7] *Ib.* cxix. 185.
[8] Friedel, *ib.* cxxxiv. 262.

dimethyl-methylene chloride (dichloracetone chloride)[1] or its isomeride tetrachlor-glycide (p. 356). The last-named compound yields in addition propylene,[2] and probably the iso-allylene described below. For the preparation of methyl-acetylene propylene bromide is used, and the method corresponds exactly to that by which acetylene is prepared from ethylene bromide.[3]

Allylene is a gas possessing a strong smell, which, however, is less unpleasant than that of acetylene. It takes fire readily, and burns with a very smoky flame. It combines slowly with fuming hydrochloric acid, forming dimethylmethylene chloride, whilst it is absorbed by highly-concentrated hydrobromic acid with formation of dimethylmethylene bromide and a little $\beta$-brompropylene.[4] If concentrated hydriodic acid be poured into a flask filled with allylene, *dimethyl-methylene iodide*, $CH_3CI_2.CH_3$, is produced, a heavy liquid which boils, with considerable decomposition, at 147°—148°,[5] and when acted on by silver oxide is transformed into acetone.[6] By the direct union of allylene with water, in presence of mercuric bromide, acetone is readily formed (see Part I. 568). Potassium permanganate oxidizes allylene in the cold, yielding formic, oxalic, and malonic acids. An aqueous chromic acid solution, on the other hand, converts it into propionic acid (Berthelot). When allylene is gently heated with sodium, it is decomposed with separation of carbon and hydrogen and formation of sodium acetylide.[7]

788 *Metallic Compounds of Allylene.* If sodium be covered with ether, then cooled in a freezing mixture, and allylene led in, the gas is absorbed in considerable quantity, and after standing for a few days *sodium-allylene*, $C_3H_3Na$, is formed, together with propane:[8]

$$5C_3H_4 + 4Na = 4C_3H_3Na + C_3H_8.$$

It is a colourless crystalline powder which becomes resinous in the air, and frequently takes fire on exposure.

When allylene is passed into a solution of cuprous chloride in ammonia, a yellow, flocculent precipitate of *cuprous allylide*, $(C_3H_3)_2Cu_2$, is thrown down. This becomes incandescent when

[1] Borsche and Fittig, *Ann. Chem. Pharm.* cxxxiii. 119.
[2] Pfeffer and Fittig, *ib.* cxxxv. 366.
[3] Liebermann, *Ann. Chem. Pharm.* cxxxv. 266.
[4] Reboul, *Ann. Chim. Phys.* [5], xiv. 465.
[5] Oppenheim, *Zeitsch. Chem.* 1865, 719; Semenow, *ib.* 1865, 725.
[6] Sorokin, *Zeitsch. Chem.* 1871, 264.
[7] Berthelot, *Ann. Chim. Phys.* (4) ix. 935.
[8] Lagermark, *Journ. Russ. Chem. Ges.* xii. 288.

heated, and on treatment with hydrochloric acid evolves allylene. It dissolves in ammonia which contains ammonium chloride in solution, and this explains the fact that when cuprous chloride is dissolved in hydrochloric acid, and the solution then saturated with ammonia, this liquid absorbs allylene, but does not yield any precipitate with it. The composition of copper-allylide has not been exactly determined, but it probably corresponds with that of the following compound.

*Silver-Allylide*, $C_3H_3Ag$. When allylene is passed into an ammoniacal silver solution, this compound is formed as a white exceedingly light precipitate, consisting of microscopic needles. This changes colour on standing, and more quickly when in the moist state, becoming at first reddish-yellow and then green, and, as in the case with silver chloride, this change of colour is not accompanied by any substantial alteration in the composition of the compound.

This substance is decomposed by mineral acids and by sulphuretted hydrogen, allylene being evolved. It deflagrates when heated, frequently at so low a temperature as 150°, with separation of spongy charcoal.

By the action of an aqueous solution of iodine and iodide of potassium, allylene is converted into *iodallylene*, $C_3H_3I$. This is a liquid which boils at 98°, possesses a penetrating odour, and strongly attacks the eyes and mucous membranes. It is retransformed into allylene when treated with zinc and hydrochloric acid (Liebermann).

789 *Haloid Ethereal Salts of Allylene.* The dichloracetone chloride already described is *allylene tetrachloride*, $CH_3.CCl_2.CHCl_2$. It is obtained by heating together for some time phosphorus pentachloride and dichloracetone (Part I. p. 571). It is an oily liquid which has a peculiar but not unpleasant smell, and boils at 153°.

*Allylene Dibromide*, $C_3H_4Br_2$, is obtained, together with the compound next described, by acting on allylene with bromine,[1] and is also formed when brompropylene bromide is heated with silver acetate.[2] It is a heavy liquid, possessing an aromatic odour, and boiling at 130°—132°.

*Allylene Tetrabromide*, $C_3H_4Br_4$, boils with partial decomposition at 225°—230°, but under a diminished pressure distils unchanged.

[1] Oppenheim, *Ann. Chem. Pharm.* cxxxii. 126.
[2] Linnemann, *ib.* cxxxvi. 56.

*Allylene Di-iodide*, $C_3H_4I_2$, is formed when allylene is exposed to sunlight in contact with a solution of iodine in potassium iodide. It is an oily liquid which boils at 198°.[1]

*Iodallylene Di-iodide*, $C_3H_3I_3$, is obtained by shaking up silver allylide with an ethereal solution of iodine so long as this is decolorized, then adding a quantity of iodine equal to that already used, and afterwards allowing the mixture to stand until the colour of the iodine has disappeared. It crystallizes in long needles which readily decompose with separation of iodine (Liebermann).

*Iso-allylene*, or *Allene*, $CH_2{=}C{=}CH_2$, is formed by the electrolysis of the potassium salt of itaconic acid, $C_3H_4(CO_2H)_2$, and is a gas which, in smell, resembles allylene, but it does not precipitate ammoniacal silver or copper solution.[2]

The hydrocarbon obtained by Hartenstein from dichlorhydrin is doubtless identical with iso-allylene. When this latter is heated with phosphorus pentachloride, *β-chlorallyl chloride*, $CHCl{=}CH{-}CH_2Cl$, is formed, a liquid having a pleasant though somewhat pungent odour, and boiling at 109°. When treated with sodium, in the presence of benzene, it yields a gas which likewise yields no precipitate with ammoniacal silver solution.

Iso-allylene combines with bromine to form *iso-allylene tetrabromide*, $C_3H_4Br_4$, a compound which dissolves readily in ether and crystallizes in tablets melting at 195.°[3]

## BUTINE COMPOUNDS.

790 *Ethyl-acetylene*, $CH_3.CH_2.C{\equiv}CH$, is obtained from ethyl-methyl-ketone by a reaction which has already been described (Part I. p. 182). It boils at 18°, has a pungent odour, and gives, with an ammoniacal silver solution, a white, and with one of cuprous chloride, a yellow, precipitate. It forms with bromine the crystalline tetrabromide.[4]

*Crotonylene*, $C_4H_6$, was obtained by Caventou by heating brom-butylene with sodium ethylate. It is a liquid which boils between 18° and 24°, possesses a pungent odour somewhat

[1] Oppenheim, *Bull. Soc. Chim.* iv. 434.
[2] Aarland, *Journ. Prakt. Chem.* [2], vi. 256.
[3] Hartenstein, *Journ. Prakt. Chem.* [2], vii. 310.
[4] Bruglants, *Ber. Deutsch. Chem. Ges.* viii. 410.

resembling that of the leek, and the density of its vapour is 1·936. It combines with bromine to yield *crotonylene tetrabromide*, $C_4H_6Br_4$, a white, crystalline body volatilizing somewhat readily in the air.[1]

The butylene dibromide, which was used by Caventou for the preparation of the brom-butylene, was obtained by fractional distillation from the mixture of bromides which is got by passing into bromine the gas obtained by heating to redness the vapour of fermentation—amyl alcohol. This gas contains, as we now know, isomeric butylenes. The question, therefore, presented itself as to which of these yields the crotonylene. Butlerow expressed the opinion that it could not be derived from isobutylene, $(CH_3)_2C{=}CH_2$, except on the supposition that crotonylene contains free combining units, and this appeared to him to be improbable. To test this theory he heated brom-isobutylene with sodium ethylate and obtained, not crotonylene, but ethyl-crotyl ether :[2]

$$(CH)_2C{=}CHBr + NaOC_2H_5 = (CH_3)_2C{=}CHOC_2H_5 + NaBr.$$

J. Lermontoff then prepared crotonylene from $\beta$-butylene dibromide, $CH_3.CHBr.CHBr.CH_3$, and Almedingen showed that the olefines thus obtained are condensed by sulphuric acid to hexmethyl-benzene, $C_6(CH_3)_6$.[3] Hence it follows that crotonylene is dimethyl-acetylene, $CH_3.C{\equiv}C.CH_3$.

791 *Butine*, $C{=}H_2CH.CH{=}CH_2$. When erythrite, $C_4H_6(OH)_4$, is heated with concentrated formic acid to 230°, butine is formed, together with water, carbon dioxide, and the formate $C_4H_6(CHO_2)OH$.[3] It is also found in the liquid formed by the condensation of coal-gas,[4] and is a liquid boiling about 20°.

*Butine Tetrachloride*, $C_4H_6Cl_4$, is formed by the direct combination of butine and chlorine, and also by the action of phosphorus pentachloride on erythrite. It crystallizes in prisms which melt at 73°.[5]

*Butine Tetrabromide*, $C_4H_6Br_4$, forms white needles or rhombic plates, which melt at 116°, and sublime when more strongly heated.

By passing the vapour of amyl alcohol through a red-hot tube and leading the evolved gas into bromine, Caventou

[1] *Ann. Chem. Pharm.* cxxvii. 347.
[2] *Zeitsch. Chem* [2], vi. 523.
[3] *Ber. Deutsch. Chem. Ges.* xiv. 2073.
[4] Henninger, *Ber. Deutsch. Chem. Ges.* vi. 70.
[5] Henninger, *Bull. Soc. Chim.* xxxiv. 194.

obtained a product containing a tetrabromide which crystallizes in needles and melts at 114°—115°,[1] and is, therefore, probably butine tetrabromide, but certainly not crotonylene tetrabromide, as it is not perceptibly volatile in the air. He pointed out, moreover, that the hydrocarbon which these crystals yield is not absorbed by ammoniacal cuprous chloride.[2]

## PENTINE COMPOUNDS.

792 *Propyl-Acetylene*, $CH_3.CH_2.CH.{\equiv}CH$, is obtained from methyl-butyl ketone, and is a mobile liquid which boils at 48°—49°, and has an alliaceous penetrating smell. It combines with bromine, forming a liquid dibromide which boils at 190°, and a liquid tetrabromide which boils at 275°, and does not solidify at —15°. Its silver compound, $C_5H_7Ag$, is a white, and its copper compound a yellow, precipitate.[3]

*Isopropyl-Acetylene*, $(CH_3)_2CH.C{\equiv}CH$, can be obtained by the reaction already described, from valeraldehyde,[4] and from isopropylethylene.[5] It is a liquid possessing a penetrating smell, boils at 28°—29° and at 0° has a specific gravity 0·6854.[6] It forms with bromine a liquid dibromide and tetrabromide. Chromic acid solution oxidizes it to isobutyric acid, acetone and acetic acid.[7] Its copper compound is yellow, and the silver compound, $C_5H_7Ag$, is white. The latter dissolves slightly in ammoniacal silver solution, and likewise in absolute alcohol, from which it crystallizes in small prisms.

*Methyl Ethyl Acetylene*, $CH_3.C{\equiv}C.C_2H_5$. On heating the dibromide prepared from commercial amylene, with alcoholic potash, Reboul obtained a liquid having a penetrating smell, and boiling at about 44°—46°, which he termed valerylene.[8] This was evidently a mixture which contained methylethylacetylene. Eltekow obtained the latter in the pure state by treating the crude amylene with sulphuric acid, converting the undissolved part (p. 241) into the bromide, and then decomposing this with potash. The product contains isopropylacetylene, which is

[1] *Ann. Chem. Pharm.* cxxvii. 93.
[2] *Ib.* cxxvii. 347.
[3] Bruylants, *Ber. Deutsch. Chem. Ges.* viii. 411.
[4] *Ib.* 406 and 413.
[5] Eltekow, *ib.* x. 707; Flawitzky and Krylow, *ib.* x. 1102.
[6] *Ib.* xi. 1939.
[7] *Ber. Deutsch. Chem. Ges.* x. 2240.
[8] *Ann. Chem. Pharm.* cxxxi. 238.

removed by means of ammoniacal silver solution, when the methyl-acetylene remains behind. It is a liquid which boils at 51°—52°, and is oxidized by aqueous chromic acid to acetic and propionic acids.[1]

Valerylene unites with bromine, forming a dibromide and tetrabromide, both of which are liquid. If the first of these be heated with alcoholic potash solution, valylene, $C_5H_6$, is formed. This is an alliaceous smelling liquid, which boils at 50°, and forms by union with bromine a crystalline hexbromide. Its silver compound, $C_5H_5Ag$, is a white, and its cuprous compound, $(C_5H_5)_2Cu_2$, a yellow precipitate (Reboul).

## HEXINE COMPOUNDS.

793 *Hexoylene*, $C_6H_{10}$, was prepared by Caventou from the hexane of petroleum oil, by converting the dibromhexane prepared from this, into bromhexylene, and then heating this latter with sodium ethylate.[2] It boils at about 80° and forms a dibromide and tetrabromide, both of which are liquid.[3] The hexoylene prepared by Hecht from the hexylene got from mannite is probably identical with this. This hexoylene boils at 80°—83°, unites readily with bromine to form a dibromide, but forms a tetrabromide only with difficulty. It is oxidized by chromic acid solution to acetic and butyric acids.[4]

A hydrocarbon of the same composition occurs in the light coal-tar oils. This has not as yet been obtained pure, but its tetrabromide crystallizes from hot alcohol in long white needles, which melt at 112°, and boil at 318°.[5]

794 *Diallyl* or *Hexine*, $CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$, was first obtained by Berthelot by the action of sodium on allyl iodide.[6] Wurtz recommends instead of sodium an alloy of this with twice its weight of tin.[7] It may be more simply prepared by bringing allyl iodide in contact with zinc, and a little ethyl formate.[8] It is also easily formed when mercury allyl iodide is subjected to

[1] *Ber. Deutsch. Chem. Ges.* x. 1904 and 2057.
[2] *Ann. Chem. Pharm.* cxxxv. 126.
[3] Reboul and Truchot, *ib.* cxliv. 246.
[4] Hecht, *Ber. Deutsch. Chem. Ges.* xi. 1050.
[5] Schorlemmer, *Journ. Chem. Soc.* xix. 356.
[6] *Ann. Chim. Phys.* [3] xlviii. 294.
[7] *Ib.* [4] iii. 129.
[8] Sorokin, *Ber. Deutsch. Chem. Ges.* xii. 383.

dry distillation,[1] or better when this latter is decomposed with potassium cyanide and the diallyl then distilled off.[2]

$$2C_3H_5HgI + 2KCN = C_6H_{10} + Hg + Hg(CN)_2 + 2KI.$$

Diallyl is a mobile liquid possessing a penetrating ethereal and alliaceous smell. It boils at 59°, and at 17° has a specific gravity of 0·6872, whilst that of its vapour is 2·92. By oxidation with acidified potassium permanganate solution, it yields succinic acid as chief product,[3] as might be indeed expected from its constitution. Concentrated sulphuric acid acts powerfully on diallyl, polymeric hydrocarbons of the formula $C_nH_{2n-4}$ being formed, together with tarry products. These hydrocarbons are obtained in larger quantity if the diallyl be first diluted with petroleum spirit.[4] Similar hydrocarbons are produced when sulphuric acid acts on coal-tar naphtha obtained from cannel coal, the products having also the formula $C_nH_{2n-4}$.[5]

*Monochlorhexine*, $C_6H_9Cl$, is formed together with the dichloride, $C_6H_{10}Cl_2$, by the action of phosphorus pentachloride on allyl acetone, $CH_3.CO.CH_2.CH_2CH{=}CH_2$, which is a product of decomposition of ethyl allyl acetacetate (p. 412). Monochlorhexine boils at about 120° and it is transformed when heated with alcoholic potash into *diallylene* or *hexone* $CH{\equiv}C.CH_2.CH_2.CH{=}CH_2$, a liquid which boils at 78°, and yields a white silver, and a yellow cuprous, compound.[6]

*Hexine Tetrabromide*, $C_6H_{10}Br_4$, crystallizes from ether in four-sided prisms which have a camphor-like smell, melt at 63°,[7] and volatilize without decomposition. By the action of sodium it is converted again into diallyl (Berthelot and De Luca). When it is distilled over solid caustic potash, *dibromhexine*, $C_6H_8Br_2$, is formed, a liquid possessing a peculiar smell and a bitter pungent taste, and boiling at 205°—210°.[8] This unites with bromine, yielding *dibromhexine tetrabromide*, $C_6H_8Br_6$, a compound crystallizing from alcohol in pearly glistening tablets, which melt at 76°—77°.

If dibromhexine be heated with a solution of caustic potash in absolute alcohol, *dipropinyl* or *dipropargyl*, $C_6H_6$, is formed, a

[1] Linnemann, *Ann. Chem. Pharm.* cxl. 180.
[2] Oppenheim, *Ber. Deutsch. Chem. Ges.* iv. 672.
[3] Sorokin, *Ber. Deutsch. Chem Ges.* xii. 2096.
[4] Jekyll, *Chem. News.* xxii. 221.
[5] Schorlemmer, *Journ. Chem. Soc.* xix. 356.
[6] Henry, *Jahresb.* 1878, 379.
[7] Tollens and Wagner. *Ber. Deutsch. Chem. Ges.* vi. 589.
[8] Henry, *Journ. Prakt. Chem.* [2] viii. 57.

mobile highly refractive liquid, which has a penetrating odour, and boils at about 85°. It combines energetically with bromine, yielding the tetrabromide $C_6H_6Br_4$, a thick viscous liquid, which combines with more bromine, slowly in the cold and quickly on heating, forming *dipropinyl octobromide*, $C_6H_6Br_8$, a compound possessing a weak camphor-like smell, melting at 140°—141°, and crystallizing from carbon disulphide in hard triclinic prisms or tables.

*Silver Dipropinyl*, $C_6H_4Ag_2+2H_2O$, is formed as a white amorphous precipitate, which in the dry state detonates when heated to 100°.

*Cuprous Dipropinyl*, $C_6H_4Cu_2+2H_2O$, is a yellow coloured explosive precipitate which when ignited burns with a green flame, evolving showers of sparks.

Dipropinyl contains two atoms of hydrogen, capable, it will be seen, of replacement by metals, and has accordingly the following constitution :[1]

$$CH{\equiv}C.CH_2.CH_2.C{\equiv}CH.$$

*Hexine Tetra-iodide*, $C_6H_{10}I_4$, is produced when diallyl is gently heated with iodine. It forms colourless crystals, which, however, soon become coloured, melts above 100°, and has an odour resembling that of ethylene iodide (Berthelot and De Luca).

*Hexine Tetranitrate*, $C_6H_{10}(NO_2)_4$ separates out in white crystals when nitrogen tetroxide is slowly passed into a mixture of diallyl and absolute ether cooled by a mixture of ice and salt.[2]

Diallyl also combines readily with the hydracids. By union with two molecules of the hydracid, pseudohexylene compounds are formed, whilst when diallyl combines with only one molecule compounds of methylisocrotyl are produced.

## Pseudohexylene Compounds.

795 *Pseudohexylene Chloride*, $C_6H_{12}Cl_2$. This compound, also known as diallyl dihydrochloride, is formed, together with the monohydrochloride or methyl-isocrotyl chloride, when diallyl is

[1] Henry, *Ber. Deutsch. Chem. Ges.* vi. 955 ; vii. 21.
[2] Henry, *ib.* ii. 279.

heated for some hours to 100° with fuming hydrochloric acid. It is an oily liquid boiling between 170° and 180°.[1]

*Pseudohexylene Iodide*, $C_6H_{12}I_2$, is obtained in a corresponding way to the chloride, and is a heavy liquid, which decomposes on heating. When brought in contact with silver acetate suspended in ether, *pseudohexylene diacetate*, $C_6H_{12}(C_2H_3O_2)_2$, is formed, a thick, aromatic-smelling liquid which boils at 225°—230°. At the same time the *monacetate*, $C_6H_{12}(OH)C_2H_3O_2$, is formed, and this boils at 210°.

*Pseudohexylene Glycol*, $C_6H_{12}(OH)_2$, is obtained by decomposing the above mixture of acetates with potash. It forms a syrupy liquid, which is soluble in water and boils at 212°—215° (Wurtz).

*Pseudohexylene Oxide*, $C_6H_{12}O$, is formed, together with some methyl-isocrotyl alcohol, by acting with silver oxide on the iodide, or with sulphuric acid on diallyl, diluted with petroleum ether (p. 466), in which latter case it is dissolved in the acid, together with polymerides of diallyl, and is separated by means of water. It is a mobile liquid, which boils at 93°, and has a refreshing peppermint-like smell. When it is heated with hydriodic acid, a hexyl iodide is formed, which boils at 165°—167°, and yields normal hexane by the action of zinc and hydrochloric acid.

*Pseudohexylene Chlorhydrate*, $C_6H_{12}(OH)Cl$, is a heavy, oily liquid formed by the union of diallyl and hypochlorous acid (Henry).

## Methyl-Isocrotyl Compounds.

796 *Methyl-Isocrotyl Chloride*, $C_6H_{11}Cl$, boils at 130°—140°, and as yet has not been obtained pure.

*Methyl-Isocrotyl Iodide*, $C_6H_{11}I$, is formed together with pseudohexylene iodide, and is a liquid boiling at 164°—166°.

*Methyl-Isocrotyl Monacetate*, $C_6H_{11}(C_2H_3O_2)$, is obtained together with the diacetate described above, and is a pleasantly-smelling liquid which boils at 154°—155°.

*Methyl-Isocrotyl Alcohol*, $C_6H_{11}OH$, is obtained by the decomposition of the acetate with caustic potash, and is a pleasantly-

[1] Wurtz, *Ann. Chim. Phys.* [4], iii. 129.

smelling liquid which boils at 140°, and at 0° has a specific gravity of 0·8604 (Wurtz). As has already been stated, this compound, which is also known as diallyl hydrate, is undoubtedly identical with the alcohol obtained from methyl-isocrotyl ketone, which has already been described (p. 412).

## HEPTINE COMPOUNDS.

797 *Pentyl-Acetylene* or *Oenanthylidene*, $C_5H_{11}C{\equiv}CH$, was first obtained by Limpricht from oenanthol (heptaldehyde), and is an alliaceous smelling liquid, which boils at 106°—108°, and forms a liquid dibromide and tetrabromide.[1] Its silver compound is formed as a white, and its cuprous compound as a yellow, precipitate.[2]

*Tetramethyl-Isoallylene*, $(CH_3)_2C{=}C{=}C(CH_3)_2$, has been prepared by Henry from diisopropyl ketone. It is a liquid which boils at about 70°, yields no metallic compounds, and has a very unpleasant smell.[3]

*Methyl-Propyl-Isoallylene*, $CH_3.CH{=}C{=}CH.C_3H_7$, occurs as one of the constituents of resin spirit, and is a liquid boiling between 103° and 104°. It yields a volatile tetrabromide, and unites with water to form the glycol, $CH_3.CH{=}C(OH).CH(OH)C_3H_7 + H_2O$, which forms brilliant crystals, and loses its water at 100°. The anhydrous compound melts at 89°·5, and boils at 195°·6. When it or the hydrocarbon is oxidized with nitric acid, dinitroheptylene, $C_7H_{12}(NO_2)_2$, is formed, together with carbon dioxide, acetic acid, butyric acid, and succinic acid. This nitro-compound crystallizes from alcohol in glistening tables which melt at 182°.[4]

[1] Rubien, *Ann. Chem. Pharm.* cxlii. 294.
[2] Bruylants, *Ber. Deutsch. Chem. Ges.* viii. 409.
[3] *Ber. Deutsch. Chem. Ges.* viii. 400.
[4] Morris, *Journ. Chem. Soc.* 1882, i. 167.

The higher homologues of this series have been but little examined. Of these the following are known:

| | | B.P. |
|---|---|---|
| [1] Caprylidene | $C_8H_{14}$ | 133°—134° |
| [2] Rutylene | $C_{10}H_8$ | 150° |
| [3] Dipropylbutine | | 165° |
| [4] Decenylene | | |
| [5] Nonyl-acetylene | $C_{11}H_{20}$ | 198°—202° |
| [6] Benylene | $C_{15}H_{28}$ | 223°—228° |
| [7] Cetenylene | $C_{16}H_{30}$ | 280°—285° |
| [8] Eikosylene | $C_{20}H_{38}$ | 314°—315° |

These are all liquid at the ordinary temperature. Besides the above a number of other hydrocarbons are known, having the general formula $C_nH_{2n}$—2, but belonging to other series.

[1] Rubien, *Ann. Chem. Pharm.* cxlii. 299.
[2] Bauer, *ib.* cxxxv. 344.
[3] Reformatsky, *Journ. Prakt. Chem.* [2], xxvii. 389.
[4] Reboul and Truchot, *ib.* cxliv. 248.
[5] Giesecke, *Zeitsch. Chem.* 1870, 431; Bruylants, *Ber. Deutsch. Chem. Ges.* viii. 413.
[6] Bauer and Verson, *Ann. Chem. Pharm.* cxlvii. 252.
[7] Chydenius, *ib.* cxliii. 268.
[8] Lippmann and Hawiliczek, *Ber. Deutsch. Chem. Ges.* xii. 69.

# ALCOHOLS OF THE SERIES $C_nH_{2n-2}O$.

## PROPINYL COMPOUNDS.

798 These stand in the same relation to allylene, as the allyl compounds do to propylene. They contain the monovalent radical, *propinyl*, $CH{\equiv}C{-}CH_2{-}$, in which one of the atoms of hydrogen may be replaced by silver, and on this account Liebermann has given to it the name of *propargyl*.[1]

*Propinyl Alcohol*, $C_3H_3.OH$, is formed by heating $\beta$-bromallyl alcohol with caustic potash and a little water. The liquid is then saturated with carbon dioxide, and, after the addition of some water, is subjected to distillation. The alcohol is separated from the distillate by means of carbonate of potash and is then dried over caustic lime.[2] It is a liquid possessing a pleasant smell, boiling at 114°—150°, and having a specific gravity of 0·9628 at 21°. It combines with hydrobromic acid forming bromallyl alcohol, whilst with bromine it forms dibromallyl alcohol. With ammoniacal silver solution it gives a white precipitate of $C_3H_2Ag(OH)$, which blackens on exposure to light, and burns explosively when gently heated. The cuprous compound, $Cu_2(C_3H_2OH)_2$, is a yellow explosive precipitate, which is decomposed by dilute acids with re-formation of the alcohol; on treatment with nitric acid it takes fire.

When the alcohol is heated with caustic potash the following reaction takes place:

$$CH\ \ C.CH_2.OH + HOK = CH\ \ CH + CHO.OK + H_2.$$

*Ethyl-Propinyl Ether*, $C_2H_5.O.C_3H_3$, was prepared by Liebermann[3] by boiling tribromhydrin or brompropylene bromide with alcoholic potash solution. It may also be prepared in the

[1] *Ann. Chem. Pharm.* cxxxv. 278.
[2] Henry, *Ber. Deutsch. Chem. Ges.* v. 569; vi. 728.
[3] *Loc. cit.*

same way from trichlorhydrin,[1] chlorpropylene bromide, chlordibromhydrin,[2] epichlorhydrin, allylene dibromide,[3] or ethyldibromallyl ether.[4] It is a liquid which possesses a penetrating smell, boils at 80°, and at 7° has a specific gravity of 0·83.

When concentrated silver nitrate solution is added to a solution of this ether in alcohol, a crystalline precipitate is formed of $(C_3H_2AgOC_2H_5)_2AgNO_3$, and this is transformed by ammonia into the amorphous compound $C_3H_2AgOC_2H_5$. An ammoniacal solution of silver chloride forms, with the ether, the compound $(C_3H_2AgOC_2H_5)_2AgCl$, a white curdy precipitate, whilst the cuprous compound is yellow and amorphous.

If the amorphous silver compound be treated with a solution of iodine in potassium iodide, *ethyl-iodpropinyl ether*, $C_2H_5.O.C_3H_2I$, is formed, an oily liquid having an unpleasant smell; it solidifies on cooling, and combines with one molecule of bromine or iodine, forming oily compounds.

Exactly as allylene unites with water in the presence of mercury bromide to form acetone, so ethyl-propinyl ether combines with water yielding the ether $CH_3.CO.CH_2.OC_2H_5$, which is a liquid boiling at 128°, and possessing a peculiar smell and burning taste. The corresponding *pyruvyl alcohol*, $CH_3.CO.CH_2OH$, which stands in the same relation to pyroracemic acid as alcohol does to acetic acid, is obtained by a similar reaction from propinyl alcohol, but it has not been more closely examined.[5]

*Propinyl Chloride*, $C_3H_3Cl$, is formed by the action of phosphorus trichloride on the alcohol, and is a very mobile liquid, which has an unpleasant smell. It boils at 65°, and at 5° has a specific gravity of 1·0454.[6]

*Propinyl Bromide*, $C_3H_3Br$, is prepared from the alcohol and phosphorus tribromide. It boils at 88°—90°, and has at 11° a specific gravity of 1·59. A certain quantity of the additive product, $C_3H_4Br_2$, is always formed together with the bromide. Propinyl bromide unites with bromine to form the liquid products $C_3H_3Br_3$ and $C_3H_3Br_5$.[7]

*Propinyl Iodide*, $C_3H_3I$, crystallizes from alcohol in fine, in-

[1] Baeyer, *Ann. Chem. Pharm.* cxxxviii. 196.
[2] Oppenheim, *ib.* Suppl. vi. 372.
[3] Liebermann and Kretschmer, *ib.* clviii. 230.
[4] Henry, *Ber. Deutsch. Chem. Ges.* v. 274.
[5] Henry, *Compt. Rend.* xciii. 421.
[6] Henry, *Ber. Deutsch. Chem. Ges.* viii. 398.
[7] *Ib.* vi. 728; vii. 761.

terlaced needles, which turn brown in the light, melt at 48°—49°, and decompose when more strongly heated.[1]

*Propinyl Acetate*, $C_3H_3.(OC_2H_3O)$, is formed by the action of acetyl chloride on the alcohol, and is a somewhat unpleasantly smelling liquid, which boils at 124°—125°, and at 12° has a specific gravity of 1·0031.[2] In presence of mercury bromide it readily combines with water, forming *pyruvyl acetate*, $CH_3.CO.CH_2.O.C_2H_3O$, a compound which is also formed by heating monochloracetone with potassium acetate; it is a liquid boiling at about 175° and possessing a refreshing smell.[3]

It is remarkable that whilst the allyl compounds boil at the same temperature as the corresponding propyl compounds, and therefore, the loss of two atoms of hydrogen has no influence on the volatility, a further separation of 2 atoms of hydrogen raises the boiling-point, inasmuch as the propinyl compounds boil from 18° to 20° higher than the corresponding compounds of the two other series (Henry).

Propinyl alcohol is the only primary alcohol of this series known. One secondary, and several tertiary alcohols, have, however, been prepared.

799 *Diallyl Carbinol*, $(C_3H_5)_2CH.OH$. For the preparation of this, a mixture of one volume of ethyl formate and two volumes of allyl iodide is added to an excess of zinc, when a brisk reaction sets in. The product is allowed to stand overnight, and then a large quantity of water is added, which acts quietly upon it and hardly causes any evolution of gas. The alcohol is then obtained by distillation and is dried over potassium carbonate. The formation of the diallyl carbinol doubtless takes place by the following reactions. Allyl zinc iodide is first formed, and this unites with the ethyl formate:

$$COH(OC_2H_5) + 2C_3H_5ZnI = Zn(OC_2H_5)I + C(C_3H_5)_2H.OZnI.$$

And the latter compound is decomposed by water thus:

$$C(C_3H_5)_2H.OZnI + H_2O = C(C_3H_5)_2H.OH + Zn(OH)I.$$

Diallyl carbinol is an aromatic smelling liquid which boils at 151°, and at 0° has a specific gravity of 0·8758.[4] Phosphorus pentachloride transforms it into the chloride $C_7H_{11}Cl$, which smells of turpentine, and boils, with decomposition, at 144°. On

[1] *Ber. Deutsch. Chem. Ges.* viii. 398.
[2] *Ib.* vi. 729.
[3] *Ib.* v. 966; xiv. 2272.
[4] M. Saytzew, *Ann. Chem. Pharm.* clxxxv. 129; Kanonikow and A. Saytzew, *ib.* clxxxv. 148.

treatment with alcoholic potash this yields *heptone*, $C_7H_{10}$, a liquid which smells like petroleum, boils at 115°, and unites with bromine forming an oily hexbromide.

*Methyl Diallyl Carbinol*, $(C_3H_5)_2C(CH_3)OH$, is prepared from ethyl acetate, allyliodide and zinc, and is a peculiarly smelling liquid, which boils at 158°·4, and has at 0° a specific gravity of 0·8638. Potassium permanganate oxidizes it to carbon dioxide and $\beta$-methyl-oxyglutaric acid : [1]

$$CH_3.C(OH)(CH_2.CH{=}CH_2)(CH_2.CH{=}CH_2) + 5O_2 = CH_3.C(OH)(CH_2.CO_2H)(CH_2.CO_2H) + 2CO_2 + 2H_2O.$$

Homologues of this tertiary alcohol are obtained when the ethyl salts of other fatty acids are subjected to the above reaction. Up to the present the following have been prepared :

| | | B.P. |
|---|---|---|
| [2] Ethyl diallyl carbinol, | $(C_3H_5)_2C(C_2H_5)OH$ | 175°—176° |
| [3] Propyl diallyl carbinol, | $(C_3H_5)_2C(C_3H_7)OH$ | 194° |
| [4] Isopropyl diallyl carbinol, | $(C_3H_5)_2C[CH(CH_3)_2]OH$. | 182°-185° |

On oxidation with potassium permanganate these are split up in a manner analogous to methyl diallyl carbinol.

## ACIDS OF THE SERIES $C_nH_{2n-4}O_2$.

800 *Propiolic Acid*, or *Propargylic Acid*, $C_3H_2O_2$. When either dibromsuccinic acid or isodibromsuccinic acid is decomposed with an excess of alcoholic potash, *acetylene dicarboxylic acid*, $C_2(CO_2H)_2$, is produced ; this forms long crystals which contain two molecules of water and effloresce in the air.[5] It combines with nascent hydrogen forming succinic acid, and with bromine, yielding dibrom-fumaric acid.[6] When the aqueous solution of this acid is gently heated, carbon dioxide is evolved, and propiolic acid is produced :

$$CO_2H.C{\equiv}C.CO_2H = CO_2 + HC{\equiv}C.CO_2H.$$

[1] Sarokin, *Lieb. Ann.* clxxxv. 169 ; *Journ. Russ. Chem. Ges.* ix. 12 ; xi. 388.
[2] Smirensky, *Journ. Russ. Chem. Ges.* xii. 488.
[3] P. and A. Saytzew, *Lieb. Ann.* cxciii. 362.
[4] Rjabinin and A. Saytzew, *ib.* cxcvii. 70.
[5] Bandrowsky, *Ber. Deutsch. Chem. Ges.* x. 838. [6] *Ib.* xii. 2212.

On evaporating the solution this acid remains as a crystalline mass which melts at 154°.

*Potassium Propiolate*, $C_3HKO_2$, is formed when the solution of acid potassium acetylene dicarboxylate is heated. It crystallizes in glistening hexagonal prisms which detonate when heated to 105°. Its aqueous solution yields a glistening crystalline precipitate with ammoniacal silver nitrate, whilst the precipitate produced by ammoniacal cuprous chloride has a siskin-green colour. Both compounds decompose with explosion when heated.[1]

*Tetrolic Acid*, $C_4H_4O_2$, was obtained by Geuther by boiling $\beta$-chlorcrotonic acid with potash solution :[2]

$$CH_3.CCl{=}CH.CO_2H = CH_3.C{\equiv}C.CO_2H + HCl.$$

The sodium salt is formed by the direct union of sodium allylide and carbon dioxide.[3]

For the preparation of the acid, use is made of the mixture of the two ethyl chlorcrotonates obtained by the action of phosphorus pentachloride on ethyl acetacetate (p. 406), since, as Geuther has pointed out, the chlorisocrotonic acid is not attacked by boiling potash.[4]

Tetrolic acid dissolves readily in water, alcohol and ether, and crystallizes in well-formed broad tables, which melt at 76°·5. It boils at 203°, and at a few degrees above this decomposes into carbon dioxide and allylene. It is not volatile in a current of aqueous vapour. Its silver salt decomposes, even in the cold, into silver-allylide and carbon dioxide.

801 *Sorbic Acid*, $C_6H_8O_2$. When the juice which has been partially saturated with lime in the preparation of malic acid from mountain-ash berries is evaporated, it gives off a peculiar penetrating odour. G. Merck found that this is due to the presence of an oily liquid, which he termed "mountain-ash oil," and Hofmann examined this product more closely. When freshly distilled it is a bright colourless liquid, possessing a faintly aromatic odour. The vapour, however, when concentrated has a repulsive odour, and when inhaled causes stupefaction. It acts like a weak acid, but when heated with caustic potash, it passes into a crystalline well-defined acid of the same composition. This is also formed by boiling the oil with strong hydrochloric acid, or heating it

[1] *Ber. Deutsch. Chem. Ges.* xiii. 2340.
[2] *Zeitsch. Chem.* 1871, 245.
[3] Lagermark, *Journ. Russ. Chem. Ges.* xii. 290.
[4] Kahlbaum, *Ber. Deutsch. Chem. Ges.* xii. 2337.

gently with concentrated sulphuric acid. To this latter acid Hofmann has given the name of *sorbic acid*, whilst he distinguishes the oil as *parasorbic acid*.[1]

According to Fittig and Barringer, the oily product is merely impure sorbic acid, and the admixture is removed by the treatment with alkalis or acids.[2]

Sorbic acid is scarcely soluble in cold, and only moderately soluble in hot water, but dissolves easily in alcohol and ether. It crystallizes from boiling dilute alcohol in long needles, which melt at 134°·5, and boils at 228°, but decomposition then takes place, an odour like that of acrolein being given off, and a resinous mass remaining behind. Sorbic acid combines with nascent hydrogen forming hydrosorbic acid (p. 414). It also unites with either one or two molecules of bromine. Combined with hydrobromic acid it forms dibromcaproic acid, whilst with hydriodic acid it forms moniodcaproic acid.

*Diallyl-Acetic Acid*, $(C_3H_5)_2CH.CO_2H$, is obtained from ethyl diallyl-acetacetate, a peculiarly smelling oily liquid, which boils at 239°—241°, and is decomposed by potash solution yielding *diallyl acetone*, $CH_3.CO.CH(C_3H_5)_2$, boiling at 174°—175°, and possessing an unpleasant smell, together with diallyl acetic acid.[3] This latter is an oily, strongly acid, unpleasantly smelling liquid, which boils at 221°—222°, and is oxidized by nitric acid to tricarballylic acid.

Diallyl-acetic acid is also formed by heating *diallyl-malonic acid*, $(C_3H_5)_2C(CO_2H)_2$, a compound which crystallizes in long prisms, and melts at 133°.[4]

*Diallyl-Oxyacetic Acid*, $(C_3H_5)_2C(OH)CO_2H$. This compound, known as *diallyl-oxalic acid*, is obtained by the action of zinc and allyl iodide on ethyl oxalate. It crystallizes in needles, which melt at 48°·5.[5]

802 *Stearoleic Acid*, $C_{18}H_{32}O_2$, is formed by the action of alcoholic potash on dibromstearic acid obtained from oleic or elaidic acid. It crystallizes from alcohol in long prisms which melt at 48°, and distil at a higher temperature almost without decomposition. It combines with a molecule of bromine yielding liquid dibromoleic acid, and this by a further assumption of

[1] *Ann. Chem. Pharm.* cx. 129.
[2] *Ann. Chem. Pharm.* clxi. 325.
[3] Wolff, *Ann. Chem. Pharm.* cci. 49; Reboul, *Bull. Soc. Chim.* xxix. 228.
[4] Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 170.
[5] M. Saytzew, *ib.* clxxxv. 183.

bromine passes into *tetrabromstearic acid*, $C_{18}H_{32}Br_4O_2$, crystallizing in large plates which melt at about 70°.

Nitric acid oxidizes stearoleic acid to *stearoxylic acid*, $C_{18}H_{32}O_4$, which crystallizes from alcohol in small glistening plates, and melts at 86°. At the same time azelaic acid and its aldehyde are also formed.[1] Limpach was unable to obtain the last-named compound, but found, in addition to the two acids named, also pelargonic acid and nitric-oxide-pelargonic acid (Part I., pp. 660, 661).[2]

If stearoleic acid be fused with potash at a low temperature, an acid is formed which is either hypogæaic acid, $C_{16}H_{30}O_2$, or an isomeride of this; at a higher temperature myristic acid, $C_{14}H_{28}O_2$, is formed.[3]

The homologues of oleic and elaidic acid, may, like these acids themselves, be converted into acids containing less hydrogen, and these latter are also formed from the doubly substituted fatty acids. In their chemical relations these closely resemble stearoleic acid.

The following acids of this series have been prepared:

| | | | M.P. |
|---|---|---|---|
| [4] Undecolic acid | $C_{11}H_{18}O_2$ | Small plates. | 59°·5 |
| [5] Myristolic acid | $C_{14}H_{24}O_2$ | — | 12° |
| [6] Palmitolic acid, | $C_{16}H_{28}O_2$ | Needles. | 42° |
| [7] Behenolic acid, | $C_{22}H_{40}O_2$ | Needles. | 57° 5 |

*Linoleic Acid*, $C_{16}H_{28}O_2$, occurs as glyceride in linseed oil, and other drying oils (p. 478). Sacc was the first to point out that this acid differs from the oleic acid contained in other oils and fats, but he did not succeed in obtaining it in the pure state.[8] It was then subjected to a more careful examination by Schüler who saponified linseed oil with soda solution, and precipitated the soap with calcium chloride. From the well-washed precipitate the calcium linoleate was dissolved by ether. The ethereal solution was then decomposed by means of hydrochloric acid, and the ether removed in a current of hydrogen. The residual acid had a dark yellow colour, and for the purpose of purification was dissolved in alcohol, the solution saturated with ammonia, and then precipitated by barium chloride. The barium linoleate thus obtained was re-crystallized from ether, and then converted

[1] Overbeck, *Ann. Chem. Pharm.* cxl. 39.
[2] *Ib.* cxc. 297.
[3] Marasse, *Ber. Deutsch. Chem. Ges.* ii. 359.
[4] Kraft, *ib.* xi. 1414.
[5] Masino, *Ann. Chem. Pharm.* ccii. 175.
[6] Schröder, *ib.* cxliii 27.
[7] Haussknecht, *ib.* cxliii. 41.
[8] *Ann. Chem. Pharm.* li 221.

into the acid by a treatment corresponding to that described for the calcium salt.[1]

Linoleic acid is a thin oily liquid, which has a faint yellow colour, and refracts light powerfully. It remains liquid at —18°, and at 14° has a specific gravity of 0·9206. It possesses a faintly acid reaction, and its taste is at first pleasant, but afterwards harsh. When treated with nitrous acid, it does not yield a solid product. Schüler obtained on analysis numbers corresponding to the formula given above, and his results were confirmed by Mulder. According to Süssenguth,[2] its formula is $C_{16}H_{26}O_2$, whilst Oudemans obtained by Schüler's method an acid from poppy oil which had the same composition as that got from linseed oil.[3]

Linoleic acid is oxidized to suberic acid by means of nitric acid (Sacc). When exposed to the air it absorbs oxygen, and is finally transformed into *linoxyn*, $C_{32}H_{54}O_{11}$, a neutral, amorphous, elastic mass, which is insoluble in alcohol and ether, but swells up and dissolves in a mixture of alcohol and chloroform.[4]

The salts of linoleic acid, which are unstable and oxidize easily, have been but little examined.

*Elæomargaric Acid*, $C_{17}H_{30}O_2$. This acid, together with its isomeride, elæolic acid, occurs as glyceride in the oil from the seeds of *Elæococca Vernicia*. It forms rhombic tables which melt at 48°, and absorbs oxygen from the air and becomes resinous. Its alcoholic solution deposits on exposure to light, the isomeric compound, *Elæostearic acid*, melting at 71°. Both these acids when heated in an atmosphere of hydrogen to 175°—180° are transformed into liquid *elæolic acid*.[5]

## DRYING OILS.

803 *Linseed Oil* is obtained in large quantities from the seed of flax (*Linum usitatissimum*), especially in England, Holland, and Russia. It has a peculiar smell and taste, and contains about eighty per cent. of trilinolein, together with triolein, trimyristin, and tripalmitin (Mulder).

[1] *Ann. Chem. Pharm.* ci. 252.
[2] *Zeitsch. Chem.* 1865, 563.
[3] *Jahresb.* 1858, 304.
[4] Mulder, *ib.* 1858, 323.
[5] Cloër, *Bull. Soc. Chim.* [2], xxvi. 286 ; xxviii. 24 ; *Jahresb.* 1878, 738.

When a thin layer of the oil is exposed to the air, it takes up oxygen, the glycerin being oxidized to carbon dioxide, formic acid and acetic acid, and finally an elastic mass remains behind which is a mixture of linoxyn with the fatty acid, and oleic acid, or the oxidation products of these.

When linseed oil is boiled in presence of air, it forms linseed oil varnish, which dries more rapidly than the unboiled oil. According to Mulder, a portion of the trilinolein is thus decomposed, and the linoleic acid passes into an elastic caoutchouc-like mass, which he terms linoleic anhydride.

By continued boiling this is formed in large quantity, and a mass is obtained which may be drawn out into long threads, is very sticky, and does not produce a fatty stain on paper. It is used in the manufacture of printers' ink.

The varnish ordinarily used for oil colours is prepared by boiling linseed oil with three per cent. of litharge or red lead, when the above reaction takes place, and lead linoleate is also formed, which adds to the hardness of the varnish.

In consequence of the presence of lead, such varnish darkens after a time if exposed in places where sulphuretted hydrogen is evolved. To avoid this, a varnish free from lead may be used, prepared by using oxide of manganese. The borate serves, however, better than the oxide for this purpose. If 100 parts of linseed oil be heated with 1·5 parts of manganese borate for a quarter of an hour, not quite to the boiling point, a varnish is obtained which dries in twenty-four hours.

Linseed oil is also largely used for the preparation of oil varnishes, which are very durable, and are little attacked by heat or moisture. These are prepared by adding boiled linseed oil, which has been prepared without lead oxide, to melted amber, copal, or other gum, and then diluting with oil of turpentine.

The sulphur balsam of the pharmacopœia (*Balsamum Sulphuris s. Oleum Lini sulfuratum*), is prepared by boiling one part of flowers of sulphur with six parts of linseed oil, until it forms a reddish-brown, tough, very unpleasantly smelling mass, which is soluble in oil of turpentine. In this operation a large quantity of sulphuretted hydrogen is given off, together with other volatile products, of which one has been isolated by Anderson, and termed by him *odmyl*. This is a mobile refractive liquid, which contains sulphur. It boils at about 71°, and possesses an unpleasant alliaceous smell.[1]

[1] *Ann. Chem. Pharm.* lxiii. 370.

*Poppy Oil* is obtained from the seeds of the poppy (*Papaver somniferum*). It has a pleasant taste, and is therefore much used in some countries for cooking purposes. It is also used in the manufacture of curd soap, and for the preparation of artists' colours. It contains the glycerides of linoleic acid, oleic acid, lauric acid, myristic acid, palmitic acid, and stearic acid.

*Walnut Oil* is used for the same purposes as poppy oil, from which it differs by containing no tripalmitin or tristearin.

*Hemp Oil* is obtained in large quantity, especially in Russia, from the seed of hemp (*Cannabis sativa*). It has a greenish or brownish-yellow colour and smells strongly of hemp. It is used in the preparation of soft soap and in the manufacture of varnish for dark colours.

*Bankune Oil* (Huile de Bancoul) is prepared from the kernel of the nut of the candleberry-tree (*Aleurites triloba*), which is indigenous to the Moluccas and the South Sea Islands, but is now cultivated in other tropical countries for the sake of its nuts, which have a taste similar to walnuts, and when dried are used by the South Sea Islanders instead of candles. They yield an oil which serves excellently for the preparation of oil colours, but as yet it has come but little into European commerce.

*Chinese Wood Oil* is obtained by pressure from the seeds of *Aleurites cordata s. Elæococca Vernicia* which is indigenous to China and Japan. It is used for painting ships, for the preparation of varnish, and also in medicine.

## COMPOUNDS OF TETRAD ALCOHOL RADICALS.

Of these only the following one is known:

804 *Erythrite* $C_4H_6(OH)_4$, was prepared in 1848 by Stenhouse from several kinds of *lichen* and termed *Erythroglucin*, *Pseudorcin* or *Erythromannite*.[1] Its correct formula was afterwards determined by Strecker.[2] Lamy having about the same time described a substance to which he gave the name of *Phycite*,[3] found in the alga *Protococcus vulgaris*, frequently covering the stems of trees, &c., and closely related to the so-called red snow (*P. nivalis*). R. Wagner suggested that phycite is identical with erythrite,[4] and Lamy afterwards showed that this is the case.[5]

The lichens from which erythrite is obtained are of a species of orchella weed such as *Roccella*. These are used in the preparation of archil, and contain *erythrin*, $C_{20}H_{22}O_{10}$, which is an orsellinate of erythrite, and is decomposed into this acid and erythrite when boiled with baryta-water or milk of lime:

$$(C_8H_7O_4)_2C_4H_6(OH)_2 + 2H_2O = 2C_8H_8O_4 + C_4H_6(OH)_4$$

For the preparation of erythrite, *R. tinctoria* or *R. fuciformis* is treated with dilute milk of lime, filtered, and the solution precipitated with hydrochloric acid. The precipitate is well washed with water, and then boiled for several hours with milk of lime; it is then filtered, the solution concentrated, and the lime removed by carbon dioxide. The solution is next evaporated to a syrup, mixed with sand, and treated with ether, in order to remove orcin, $C_7H_8O_2$, which is a product of decomposition of orsellinic acid. The erythrite is extracted from the residue with water and precipitated from the concentrated solution by the addition of alcohol. It is then washed with cold

[1] *Phil. Trans.* 1848, 76; 1849, 399.
[2] *Ann. Chem. Pharm.* lxviii. 111.
[3] *Ann. Chim. Phys.* [3], xxxv. 138.
[4] *Journ. Prakt. Chem.* lxi. 125.
[5] *Ann. Chim. Phys.* [3] li. 232.

alcohol and recrystallized from its hot aqueous solution after treatment with animal charcoal.[1]

De Luynes obtained it in the following way from *R. Montagnei*. The erythrin prepared from the lichen is heated with milk of lime to 150° in an iron vessel, air being excluded. The filtrate freed from lime is concentrated in order that the orcin may crystallize out, and a mixture of orcin and erythrite is obtained from the mother-liquor, these being then separated by means of ether. The residual erythrite is dissolved in the smallest possible quantity of water and about one-third part its volume of alcohol added. The small crystals which separate out are dissolved in water, animal charcoal added, the liquid filtered, and the hot concentrated solution decomposed by adding one-fifth part its volume of alcohol, when, on cooling, fine large crystals separate out.[2]

Orcin and erythrol may also be separated by means of boiling benzene, in which the last named is insoluble.[3]

Erythrol dissolves readily in water and crystallizes in quadratic prisms which have a sweet and cooling taste. It is not fermentable by yeast and does not reduce copper salts; it melts at 120° (Hesse) and volatilizes, with partial decomposition, at about 300°. When heated with concentrated hydriodic acid it is transformed into secondary butyl iodide (Part I. p. 582), whilst when heated with concentrated formic acid to 230° it yields *butine*, $C_4H_6$, the radical of erythrite, whilst at the same time *butine glycol*, $C_4H_6(OH)_2$, a thick liquid boiling at 199°—200°, and its monoformin, $C_4H_6(OH)CHO_2$, boiling at about 190°, are also formed.[4] Phosphorus pentachloride converts erythrol into the corresponding chloride, a body already described as butine tetrachloride. When a solution of erythrol is treated with platinum black and allowed to stand in contact with air, *erythritic acid*, $C_3H_4(OH)_3CO_2H$, is produced, and this forms a deliquescent crystalline mass.[5] Dilute nitric acid oxidizes erythrite to oxalic acid and an inactive tartaric acid.

805 *Erythrol Dichlorhydrin*, or *Butine Dichlorhydrate*, $C_4H_6Cl_2(OH)_2$, is formed in feathery crystals when erythrite is heated in a current of hydrochloric acid to 120°—130°.[6] It

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* vii. 512.
[2] *Ann. Chim. Phys.* [4], ii. 399.
[3] Stenhouse, *Journ. Chem. Soc.* [2], v. 222.
[4] Henninger, *Ber. Deutsch. Chem. Ges.* v. 1059.
[5] Sell, *Zeitsch. Chem.* 1866, 12.
[6] Przibytek, *Ber. Deutsch. Chem. Ges.* xiv. 2072.

is also produced when erythrite is heated for 100 hours to 100° with ten to fifteen times the quantity of fuming hydrochloric acid (De Luynes). This result is produced more quickly if a temperature of 120°—130° be used (Przibytek). It is soluble in water, and separates from ether in small crystals which melt at 124°—125°.

*Erythrol Dibromhydrin*, $C_4H_6Br_2(OH)_2$, is obtained when erythrite is heated with hydrobromic acid and forms crystals which melt at 130° and are insoluble in water.[1]

*Acid Butine Tetrasulphate*, or *Erythrol Tetrasulphuric Acid*, $C_6H_4(SO_4H)_4$, is produced when erythrol is dissolved in chlorsulphonic acid, and forms a heavy white mass consisting of small prisms, and it yields also crystalline salts.[2]

*Butine Tetranitrate*, or *Nitroerythrol*, $C_4H_6(NO_3)_4$, is formed by dissolving erythrite in well-cooled concentrated nitric acid, and then precipitating by sulphuric acid. It is insoluble in water, but crystallizes from alcohol in large glistening plates, which melt at 61°, and when more strongly heated inflame and burn rapidly with a dull flame. The compound explodes on percussion, and is transformed by alcoholic ammonium sulphide into erythrite again.[3]

When erythrol is heated with organic acids the ethereal salts of these acids are obtained. They have, however, as yet not been closely examined.[4]

[1] Champion, *Compt. Rend.* lxxiii. 114.
[2] Claesson, *Journ. Prakt. Chem.* [2], xx. 7.
[3] Stenhouse, *Ann. Chem. Pharm.* lxxx. 225; cxx. 302.
[4] Berthelot, *Chim. org. sur les fondée sur la Synthese*, ii. 224.

# COMPOUNDS OF HEXAD ALCOHOL RADICALS.

## Mannitol, *or* Mannite, $C_6H_8(OH)_6$.

**806** The compound, formerly known as *manna sugar*, and now also termed *a-hexone alcohol*, was discovered in manna by Proust in 1806.[1] This latter consists of the evaporated sap which exudes from various species of ash (*Fraxinus ornus* and *rotundifolia*), some of which are cultivated in Southern Europe and in Calabria and Sicily. The manna which the Israelites are said to have used as bread during their wanderings in the wilderness probably exuded from the branches of the *Tamarix mannifera*, which contains no mannite but a fermentable sugar, whilst that which fell from heaven probably was the edible lichen, *Spaerothallia esculenta*, which grows in Asia Minor, Persia, North Africa, &c., is carried in masses before the wind forming a rain of manna (Luerssen).[2]

Mannite occurs widely distributed in the vegetable kingdom, being found in the roots of celery, in monkshood (*Aconitum napellus*), in the leaves of *Syringa vulgaris*, in the olive, in the bark of *Canella alba*, in the sap of the larch (*Pinus Larix*), in the sugar-cane, in various algæ, in many fungoid growths, &c. After immoderate water-drinking it is found in the urine. It is also formed in the lactic and mucous fermentations of sugar, and it may be obtained from the isomeric saccharoses, dextrose and lævulose, $C_6H_{12}O_6$, the corresponding aldehydes (see sugars, &c).

For the preparation of mannite, manna is dissolved in half its weight of boiling water, the solution clarified with white of egg and filtered boiling hot. The mannite which crystallizes out is separated from the liquor by pressure, and recrystallized from

[1] *Ann. Chim.* lxvii. 143.
[2] Beilstein, *Org. Chem.* 553.

hot water, after treatment of the solution with animal charcoal. Mannite may also be extracted from manna by boiling dilute alcohol, and the crystals which separate on cooling are then recrystallized from water or alcohol. *Agaricus integer*, a commonly-occurring fungus, may also be used as a source of mannite, it containing, in the dry state, from nineteen to twenty per cent. of this substance.

Mannite has a pleasant sweet taste, and dissolves at 16°·5 in 6·22 parts of water. It is much more readily soluble in boiling water, and crystallizes in small rhombic prisms. It is much less soluble in alcohol, and from this solution separates in needles; and it is insoluble in ether. It melts at 166°, and on prolonged fusion partially volatilizes. The aqueous solution is optically inactive, but on addition of borax becomes strongly dextro-rotatory,[1] whilst caustic soda imparts to it a lævo-rotatory power.[2] When heated with concentrated hydriodic acid, mannite is transformed into secondary hexyl iodide (Part I., p. 627).

A mixture of mannite and platinum black, moistened with water, oxidizes in the air forming *mannitic acid*, $C_5H_5(OH)_5CO_2H$, a gummy mass, and its aldehyde, $C_6H_{12}O_6$, which belongs to the class of fermentable sugars, and is known as *mannitose*.[3] This will be afterwards described, as also *saccharic acid*, $C_4H_4(OH)_4(CO_2H)_2$, formed by the oxidation of mannite with nitric acid.

807 *Mannitan*, $C_6H_{10}O_5$, is formed when mannite is heated to 200° or boiled for some time with concentrated hydrochloric acid. It is a syrupy liquid having only a slightly sweet taste, and deliquesces on exposure.[4] It has a feeble dextro-rotatory power,[5] and on long boiling partially recombines with water, forming mannite.

If mannite be heated with half its weight of sulphuric acid to 120°—125° a mannitane is produced which has strongly dextro-rotatory power, and does not re-unite with water to form mannite (Vignon). Both modifications dissolve readily in cold alcohol.

When the mannitane prepared by means of hydrochloric acid is exposed for some months in a dry atmosphere, it deposits

[1] Vignon, *Ann. Chim. Phys.* [5], ii. 440.
[2] Muntz and Aubin, *ib.* [5], x. 556.
[3] Gorup-Besanez, *Ann. Chem. Pharm.* cxviii. 257.
[4] Berthelot, *Ann. Chim. Phys.* [3], xlvii. 306.
[5] Bouchardat, *Ann. Chim. Phys.* [5], vi. 102.

crystals from which the syrupy mother-liquor may be separated by washing with absolute alcohol. Crystallized mannitane consists of monoclinic tables dissolving readily in water, and being easily transformed into mannite on boiling with this liquid.

*Mannite Dichlorhydrin*, or *a-Hexone Dichlorhydride*, $C_6H_8(OH)_4Cl_2$, is formed when mannite is heated for ten to fifteen hours at 100° with fifteen times its weight of aqueous hydrochloric acid which has been saturated at 0°. The solution is concentrated over sulphuric acid and quicklime, when the compound separates out very slowly in monoclinic crystals which melt with decomposition at 174° and are lævo-rotatory.

*Mannite Dibromhydrin*, $C_6H_8(OH)_4Br_2$, is obtained in a similar way to the foregoing compound, and closely resembles it, except in that it is insoluble in cold water, and melts at 178° with evolution of hydrobromic acid.

If these compounds be boiled with water they are converted into the *monochlorhydrin*, $C_6H_8OCl(OH)_3$, and *monobromhydrin*, $C_6H_8OBr(OH)_3$, of mannitan respectively. Both are crystalline, melt below 100°, and dissolve readily in water. If they are boiled for a longer time with water, mannite is again obtained (Bouchardat).

*Acid Sulphates of Mannite.* When mannite is dissolved in concentrated sulphuric acid, the *disulphate*, $C_6H_8(OH)_4(SO_4H)_2$,[1] and the *trisulphate*, $C_6H_8(OH)_3(SO_4H)_3$,[2] are formed. These form readily soluble salts, and on heating with water are decomposed, yielding mannite again.

*Mannite Hexasulphuric Acid*, or *a-Hexone Hexasulphate*, $C_6H_8(SO_4H)_6$, is obtained by dissolving mannite in chlorsulphonic acid:

$$C_6H_8(OH)_6 + 6ClSO_2{\cdot}OH = C_6H_8(O.SO_2{\cdot}OH)_6 + 6HCl.$$

As the product is uncrystallizable it has not as yet been obtained in the pure state, but several of its salts have been prepared. Of these *barium hexhexone sulphate*, $C_6H_8(SO_4)_6Ba_3 + 5H_2O$, is characteristic, and is obtained by neutralizing the freshly prepared aqueous solution of the acid with barium carbonate, the mixture being well cooled during the operation. On adding absolute alcohol to the solution thus obtained, the salt is thrown down as an oily liquid, which spontaneously passes

[1] Favre, *Ann. Chim. Phys.* [3], xi. 77; Berthelot, *ib.* [3], xlvii. 336.
[2] Knop and Schnedermann, *Ann. Chem. Pharm.* li. 132.

into a crystalline modification which is completely insoluble in water and acids. Similarly, if the aqueous solution of the salt be evaporated on the water-bath the insoluble forms separate out in crystalline crusts. The free acid and also the solutions of its salts are strongly dextro-rotatory. The acid in aqueous solution readily changes into the *tetrasulphate*, $C_6H_8(OH)_2(SO_4H)_4$, which has a weaker dextro-rotatory power and forms amorphous salts.[1]

808 *Nitro-mannite*, or *a-Hexone Hexnitrate*, $C_6H_8(NO_3)_6$. This compound was first obtained by Flores Domonte and Ménard,[2] and by Sobrero,[3] by acting on mannite with a mixture of concentrated nitric and sulphuric acids. Its correct composition was afterwards established by Strecker,[4] and Knop was the first to put forward the view that it is not a nitro-compound, but contains nitric acid.[5]

To prepare nitro-mannite one part of finely powdered mannite contained in a mortar is treated, in small quantities at a time, with five parts of well-cooled nitric acid of specific gravity 1·5, and the clear solution is then poured into a vessel kept cold by ice or snow, and ten parts of concentrated sulphuric acid added, the mixture being kept well stirred. After a few hours the curdy mass which is formed is brought on to an asbestos filter, the liquid filtered off, and the residue well rubbed up with water until it has only a weak acid taste. The product is then washed with hot solution of carbonate of soda, and afterwards purified by recrystallization from hot alcohol.[6]

Nitro-mannite crystallizes in needles which melt at 112°—113°, and on carefully raising the temperature they quietly decompose. If, however it be thrown on to glowing charcoal it deflagrates strongly, and when struck with a hammer it explodes more violently than fulminating mercury. Its alcoholic solution is dextro-rotatory. When treated with sulphuric acid it evolves fumes of nitric acid, and when treated with ammonium sulphide,[7] acetic acid and ice,[8] or hydriodic acid,[9] it is re-converted into mannite. Mannite is also formed when nitro-mannite is boiled for some time with a solution of acid ammonium sulphite, whilst

[1] Claesson, *Journ. Prakt. Chem.* [2], xx. 10.
[2] *Compt. Rend.* xxiv. 89 and 391.
[3] *Ib.* xxv. 21.
[4] *Ann. Chem. Pharm.* lxxiii. 59.
[5] *Journ. Prakt. Chem.* xxii. 228.
[6] Sokolow, *Journ. Russ. Chem. Ges.* xi. 136.
[7] Dessaignes, *Compt. Rend.* xxxiii. 462.
[8] Béchamp, *Ann. Chim. Phys.* [3], xlvi. 354.
[9] Mills, *Journ. Chem. Soc.* xvii. 153.

at the same time ammonium sulphate, nitrate, and nitrite are produced.[1]

If dry ammonia be passed into an ethereal solution of nitro-mannite, evolution of gas takes place, and a semi-fluid black mass separates out, which contains ammonium nitrite and nitrate, together with other bodies. If the liquid be poured off from this, the ether allowed to evaporate, and the residue crystallized from alcohol, long needles arranged in stellar groups are first deposited. These are either *hexone pentanitrate*, $C_6H_8(OH)(NO_3)_5$, or have the formula $[C_6H_8(NO_3)_5]_2O$. They melt at 77°—79°, deflagrate slightly when more strongly heated, and explode on percussion. From the alcoholic mother-liquor, water precipitates syrupy *mannitan tetranitrate*, $C_6H_8O(NO_3)_4$, which on percussion detonates more powerfully than nitro-mannite.[2]

809 *a-Hexone Hexacetate*, $C_6H_8(C_2H_3O_2)_6$, is produced, together with mannitan acetates, when mannite is heated with acetic anhydride.[3] It is best prepared by warming mannite with four times its weight of the anhydride and some zinc chloride, when a moderately brisk reaction sets in in a few moments.[4] The acetate forms rhombic crystals which melt at 119°, and are dextro-rotatory. They are insoluble in cold water, alcohol, and ether, but dissolve somewhat on heating, and very readily in acetic acid.

According to Schützenberger, the first product of the action of acetic anhydride on mannite is the compound $C_{12}H_{23}(C_2H_3O)O_{10}$, which in the pure state forms a light white mass, which has a slight sweet but somewhat bitter taste, and on saponification yields mannitan, the molecular formula of which is therefore probably $C_{12}H_{24}O_{10}$.

When mannite is heated with glacial acetic acid to 200°—220° mannitan diacetate, $C_6H_{10}(C_2H_3O_2)_2O_5$, is formed. This is a very bitter syrup, which on saponification yields acetic acid and mannitan.

By heating mannite with other fatty acids, Berthelot has obtained a series of ethereal salts of mannitan.[5]

[1] A. and W. Knop, *Journ. Prakt. Chem.* lvi. 337.
[2] Tichanowitsch, *Zeitsch. Chem.* 1864, 482.
[3] Schützenberger, *Ann. Chem. Pharm.* clx. 94; Bouchardat, *loc. cit.*
[4] Franchimont, *Ber. Deutsch. Chem. Ges.* xii. 2059.
[5] *Ann. Chim. Phys.* [3], xlvii. 315.

## Dulcitol, Dulcite, or β-Hexone Alcohol, $C_6H_8(OH)_6$.

810 In 1836, Hünefeld found that a peculiar crystalline body, termed by him *melampyrin*,[1] exists in the sap of *Melampyrum nemorosum*, and *M. vulgatum*. This body was then further examined by Eichler, who found it also in *Scrophularia nodosa*, and *Rhinanthus Christa-Galli*, but the formula assigned by him to the substance was an incorrect one.[2]

In 1848, Laurent examined certain crystalline lumps of unknown origin, which were sent from Madagascar to Paris in large masses, and found that their principal constituent was a sugar-like substance, which he considered to be a homologue of grape sugar, or of the glucoses, $C_6H_{12}O_6$, and termed it *dulcose*, assigning to it the formula $C_7H_{14}O_6$,[3] whilst Jacquelain believed its composition to be $C_5H_{12}O_5$, and termed it *dulcine*.[4] Souberan came to the conclusion that it was mannite,[5] and soon after Laurent recognized the fact that it is an isomeride of mannite.[6] Finally Gilmer showed that dulcite is identical with melampyrin and with the evonymite which Kubel found in the sap of *Evonymus Europœus*.[7]

The Madagascar manna, as the above-mentioned lumps were termed, consists almost entirely of dulcite, and this is readily extracted by treatment with hot water. Dulcite may be obtained from *Melampyrum nemorosum* by boiling the plant, dried when flowering, with water, adding milk of lime to the decoction till just alkaline, and again boiling, and then decomposing the filtered solution, after sufficient evaporation, with hydrochloric acid. The dulcite then separates out and is purified by recrystallization.

Dulcite is also formed by union of hydrogen with galactose, $C_6H_{12}O_6$, a saccharose obtained from milk-sugar, and an aldehyde of dulcite.

Dulcite has a taste less sweet than that of mannite, and is also less soluble in water, dissolving at 16°·5 in thirty-four parts of this liquid. It is but very slightly soluble in alcohol, and does not dissolve in ether. It crystallizes in monoclinic prisms which melt at 188°·5. When heated with concentrated hydriodic acid it yields the same secondary hexyl iodide as is obtained

[1] *Journ. Prakt. Chem.* vii. 233 ; ix. 47.
[2] *Jahresb.* 1856, 665.
[3] *Compt. Rend.* xxx. 41. [4] *Ib.* xxxi. 625. [5] *Ib.* xxx. 339.
[6] Laurent and Gerhardt, *Compt. Rend.* 1851, 29.
[7] *Ann. Chem. Pharm.* cxxiii. 372.

from mannite,[1] but it differs from the latter substance inasmuch as nitric acid does not oxidize it to saccharic acid, but to the isomeric mucic acid. Dulcite dissolves when warmed with concentrated hydrochloric acid, and on cooling down to 0° the compound, $C_6H_{14}O_6 + HCl + 3H_2O$, separates out in large crystals which lose hydrochloric acid on exposure to air, and are decomposed into their constituents when treated with water or alcohol. It forms corresponding compounds with hydrobromic and hydriodic acids.[2]

811 *Dulcitan*, $C_6H_{10}O_5$, is formed when dulcite is heated for some time to 200°, and is a viscous syrup, which dissolves readily in water and alcohol, but is insoluble in ether, and is perceptibly volatile at 120°. When exposed to moist air, or on heating with baryta-crystals and water to 160°, it is partially transformed into dulcite. When dulcite is heated with organic acids, ethereal salts of dulcitan are formed, some of which are crystalline and others amorphous.[3] Dulcitan differs from the isomeric mannitan by acting as a pentatomic alcohol, and it may therefore be termed *hexonyl alcohol*, $C_6H_7(OH)_5$.

*Dulcitol Dichlorhydrin*, or *β-Hexone Dichlorhydrate*, $C_6H_8(OH)_4Cl_2$, is obtained in a similar way to the corresponding mannite derivative. It crystallizes in small tables which are insoluble in water, and at 180° it splits up into hydrochloric acid and *dulcitan chlorhydrin*, or *hexonyl chlorhydrate*, $C_6H_7(OH)_4Cl$, this compound being also produced on boiling with water. It crystallizes in long easily soluble needles, which melt at 90°, and are dextro-rotatory. It readily unites with hydrochloric acid, forming again the dichlorhydrin, whilst with hydrobromic acid it yields the chlorbromhydrin $C_6H_8(OH)_4Cl\,Br$.

*Dulcitol Dibromhydrin*, $C_6H_8(OH)_4Br_2$, crystallizes in small tables, which are insoluble in cold water, whilst when dissolved in hot water they yield *dulcitan bromhydrin*, $C_6H_7(OH)_4Br$. This latter forms long very soluble needles, which melt at 143°, readily reunite with hydrobromic acid, and yield the dichlorhydrin on treatment with fuming hydrochloric acid.

If any one of the foregoing compounds, and the best for this purpose is dulcitan chlorhydrin, be heated with alcoholic ammonia, *dulcitamine*, $C_6H_8(OH_5)NH_2$, is formed. To separate this, the solution is evaporated and the hydrochloride extracted by means

[1] Wanklyn and Erlenmeyer, *Zeitsch. Chem.* 1862, 641.
[2] Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 168.
[3] Berthelot, *Chim. Org. Synth.* ii. 209.

of absolute alcohol. On then adding ether the salt crystallizes out in needles. By the action of silver oxide on the aqueous solution the free base is obtained, and this on evaporation forms a thick syrup, having a strongly alkaline reaction, absorbing carbon dioxide from the air, and decomposing ammoniacal salts.[1]

*Sulphates of Dulcitol.* According to Eichler, dulcite when dissolved in sulphuric acid yields the acid *trisulphate*, $C_6H_8(OH)_3(SO_4H)_3$, whose barium salt is amorphous. When dulcite is dissolved in chlorsulphonic acid, *acid dulcitan pentasulphate*, $C_6H_7(SO_4H)_5$, is formed. This is a syrup which on warming with water, splits up into dulcitan and sulphuric acid.

*β-Hexone Hexnitrate*, or *Nitrodulcitol*, $C_6H_8(NO_3)_6$, is obtained by dissolving one part of dulcite in five parts of fuming nitric acid, adding ten parts of sulphuric acid, and then pouring the mixture quickly into ten to fifteen parts of water.[2] The salt which separates out crystallizes from alcohol in beautiful flexible needles which melt at 85°·5. At the ordinary temperature these give off acid vapours, and when they are kept for a few months at a temperature of 35° to 40° they are transformed into the *tetranitrate*, $C_6H_8(OH)_2(NO_3)_4$, less soluble in alcohol than the former compound, and crystallizing from this solution in transparent needles.

*Acetates of Dulcitol.* When ten parts of dulcite are dissolved in a boiling mixture of twelve parts of acetic anhydride and 120 parts of glacial acetic acid, and the mixture allowed to cool, *β-hexone diacetate*, $C_6H_8(OH)_4(C_2H_3O_2)_2$, is formed. This crystallizes from hot water in thin tables which melt at 175°, and have a feeble dextro-rotatory power.

When dulcite is heated with an equal quantity of glacial acetic acid, and three times its amount of acetic anhydride, *β-hexone hexacetate*, $C_6H_8(C_2H_3O_2)_6$, is formed, and this crystallizes from boiling alcohol in leaflets which melt at 171°.

*β-Hexone Pentacetochlorhydrin*, $C_6H_8(C_2H_3O_2)_5Cl$, is obtained by heating dulcite with acetyl chloride. It forms microscopic crystals, which on boiling with alcohol are converted into *β-hexone pentacetate*, $C_6H_8(C_2H_3O_2)_5OH$, this latter crystallizing in fine needles melting at 163°. If, however, it be heated for some time to 200° a brittle resinous mass of *hexonyl pentacetate*, $C_6H_7(C_2H_3O_2)_5$, is formed.

[1] Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 197.
[2] Béchamp, *Compt. Rend.* li. 255 ; *see also* Champion, *ib.* lxxviii. 1150.

812 *Isodulcite*, $C_6H_{14}O_6$, does not occur in the free state in nature but is found as a peculiar ethereal salt belonging to the class of glucosides. On boiling with dilute sulphuric acid this splits up into isodulcite and other bodies which will be hereafter described. Isodulcite was first obtained by Hlasiwetz and Pfaundler from quercitrin, a body occurring in quercitron bark, a product contained in the bark of the *Quercus tinctoria*.[1] Liebermann and Hörmann afterwards prepared it from *Xanthorhamnin* contained in *Rhamnus infectorius* and *R. tinctoria*.[2]

Isodulcite dissolves readily in water, has a very sweet taste, and crystallizes in large, transparent, glassy, monoclinic prisms or tables, which melt at 92°—93° and are dextro-rotatory. At 100° it is converted into amorphous *isodulcitan*, $C_6H_{12}O_5$, and this on solution in water again yields isodulcite. If sodium alcoholate be added to a solution of isodulcite in absolute alcohol, the compound, $C_6H_{12}Na_2O_6$, is precipitated as a crystalline powder.[3] When isodulcite is heated with concentrated hydriodic acid, it is converted for the most part into a tarry mass, whilst at the same time a heavy liquid, containing iodine, distils over. This is a mixture of several bodies which have not as yet been separated.[4] The action of a mixture of concentrated nitric and sulphuric acids transforms isodulcite into *nitro-isodulcitan*, $C_6H_9(NO_3)_3O_5$, an amorphous and insoluble body which explodes slightly on percussion.

When oxidized with dilute nitric acid, isodulcite yields dibasic *isodulcitic acid*, $C_6H_{10}O_9$, remaining on evaporation of its solution as a syrup, from which crystalline grains separate out on standing.[5]

813 *Sorbite*, $(C_6H_{14}O_6)_2 + H_2O$, occurs in mountain-ash berries, and in the vinous liquor obtained from these by fermentation. If this latter be precipitated with lead acetate and the filtrate, after treatment with sulphuretted hydrogen, be allowed to evaporate, a syrup remains behind from which sorbite gradually separates out in crystals. It loses its water of crystallization at about 100°, and then melts at 110°—111°.[6]

814 *Pinite*, $C_6H_{12}O_5$. This compound, isomeric with mannitan,

[1] *Ann. Chem. Pharm.* cxxvii. 362.
[2] *Ib.* cxcvi. 323.
[3] Liebermann and Hörnmann, *Ber. Deutsch. Chem. Ges.* xii. 1186.
[4] Dale and Schorlemmer, *ib.* xi. 1197.
[5] Malin, *Ann. Chem. Pharm.* cxlv. 197.
[6] Boussingault, *Ann. Chim. Phys.* [4], xxvi. 376.

&c., forms the principal constituent of the pine-sugar contained in the sap of *Pinus lambertiana*, which grows profusely on the western slopes of the Sierra Nevada in California. This collects at the foot of the tree, in holes burnt into the trunk, in dark round lumps and is used by the Indians as a food.[1] Pinite is exceedingly soluble in water, has a very sweet taste, crystallizes in hard white nodules, and is dextro-rotatory.

A substance isomeric with pinite has been obtained by Eichler and termed quercite, but this, as is also probably the case with pinite itself, is not connected with the group of fatty bodies, and will be described hereafter.

[1] Berthelot, *Ann. Chim. Phys.* [3], xlvi. 76 : Johnson, *Journ. Prakt. Chem.* lxx. 246.

## CARBOHYDRATES.

**815** The above name has for some time past been given to a group of compounds which contain, in the molecule, six atoms of carbon or a multiple of this number, together with hydrogen and oxygen present in the proportion in which these elements unite to form water.

Many of the carbohydrates constitute some of the most important constituents of plants, some few are also found in the animal kingdom, whilst the larger number are well known as valuable articles of food.

They consist of several distinct isomeric groups, most of whose members exhibit active optical properties deviating the plane of polarized light either to the right (+) or to the left (—).

### I. THE SUGAR GROUP.

| *The Saccharoses.* $C_{12}H_{22}O_{11}$. | *The Glucoses.* $C_6H_{12}O_6$. |
|---|---|
| + Cane-sugar, or saccharose. | + Grape-sugar, or dextrose. |
| + Milk-sugar. | — Fruit-sugar, or levulose. |
| + Melezitose. | + Galactose. |
| + Melitose. | + Arabinose. |
| + Trehalose. | + Eucalyn. |
| + Maltose. | — Sorbin. |
| | Inosite. |
| | Scyllite. |
| | Dambose. |

The saccharoses are ether-like compounds which are converted into *glucoses* on boiling with dilute sulphuric acid :

$$O\left\{\begin{matrix} C_6H_{11}O_5 \\ C_6H_{11}O_5 \end{matrix}\right. + H_2O = 2C_6H_{12}O_6.$$

Cane-sugar, when thus treated, yields equal quantities of grape-sugar and fruit-sugar. Such a mixture is widely distributed throughout the vegetable world, and is termed *invert-sugar* because it deviates the plane of polarization to the left, the specific rotatory power of levulose being at ordinary temperatures greater than that of dextrose. Milk-sugar thus acted upon gives galactose and grape-sugar, the latter being also formed, together with eucalyn, from melitose, whilst all the other saccharoses apparently yield only grape-sugar.

Of the glucoses the first three alone have been carefully examined. They reduce ammoniacal silver solution with deposition of a metallic mirror. Grape- and fruit-sugar combine directly with nascent hydrogen to form mannitol, $C_6H_8(OH)_6$, galactose yielding the isomeride dulcite. In these respects the glucoses act as aldehydes of these alcohols, but they do not exhibit the characteristic reaction of aldehydes discovered by Hugo Schiff, and which, according to Caro, is a general one for this class of compounds.

This reaction consists in adding sulphurous acid to a solution of aniline-red until the latter is decolourized; upon the addition of an aldehyde to this colourless solution it assumes a splendid violet tint. Grape-sugar does not give this reaction, and it and its isomers may, therefore, possibly be a ketone-alcohol, $HO.CH_2(CH.OH)_3CO.CH_2.OH$.[1] On the other hand, grape-sugar yields, on oxidation, monobasic gluconic acid, $C_6H_{12}O_7$, and dibasic saccharic acid, $C_6H_{10}O_8$, whereas the above constitutional formula would point to the formation, under these conditions, of acids containing less than six atoms of carbon. It may, however, be remembered that Breuer and Zincke, in the examination of the acetic ether of acetylcarbinol, $CH_3.CO.CH_2.OH$, obtained by the action of potassium acetate upon monochloracetone, found that this, when oxidized by an alkaline solution of a cupric salt, did not yield, as was expected, pyro-racemic acid, $CH_3.CO.COOH$, but formed ordinary lactic acid, $CH_3.CH(OH)CO.OH$.[2] In a similar way grape-sugar may yield gluconic acid, and the formation of laevulinic acid (p. 249), a ketonic acid from grape-sugar, favours this view.

[1] Victor Meyer, *Ber. Deutsch. Chem. Ges.* xiii. 2344.
[2] *Ber. Deutsch. Chem. Ges.* xiii. 635.

## II. THE AMYLOSE GROUP $(C_6H_{10}H_5)_n$.

| | | |
|---|---|---|
| + Starch. | Laevulin. | Gums. |
| + Dextrin. | + Glycogen. | Cellulose. |
| − Inulin. | | |

Some of the members of this group are soluble in cold or in hot water; others soften and swell when brought in contact with water hot or cold, whilst cellulose is insoluble in water. They are all transformed by the action of acids into glucoses.

## THE SACCHAROSES.

### Cane-Sugar, $C_{12}H_{22}O_{11}$.

**816** Sugar was known to Eastern nations in early times, but was not introduced into Europe until the time of Alexander the Great, and it was at first used entirely as a medicine. Dioscorides, speaking of the different kinds of honey, says, "Some are termed sugars (*σάκχαρον*), being a solid honey found in canes (*ἐπὶ τῶν κάλαμων*), coming from India and Arabia Felix, in consistence like salt, and capable like salt of being ground to powder between the teeth." Pliny remarks on this subject, "Saccharon ex Arabia fert, sed laudatius India; est autem mel in arundinibus collectum, gummium modo candidum, dentibus fragile, amplissimum mucis avellanæ magnitudine, ad medicinæ tantum usum." The Arabians, and the physicians educated in their schools, speak of this product in similar terms. The oriental names for sugar are derived from the Sanskrit *Sharkarā*, signifying a body in the form of granules or small stones.

The cultivation of the sugar-cane spread from the far East to Arabia, Nubia, and Egypt. The Saracens extended its culture to Sicily and other islands of the Mediterranean, and the Moors introduced it into southern Spain and Portugal. In the year 1494, the sugar-cane was first planted in Madeira, and in 1495 it found its way to St. Domingo, and in 1503 to the other West Indian islands. We find it in the Brazils towards the beginning of the sixteenth century, shortly after which it was introduced largely throughout the American continent.

The importation of sugar from these localities into Europe soon made this article better known. Libavius, in his *Alchymia*,

published in 1595, mentions, "Sacchari crystallini quod candi appellant;" he recommends a plan of purifying Madeira sugar by means of albumen, and Angelus Sala in his *Saccharologia* advises the use of egg albumen and lime-water for this purpose.

817 The sugar-cane (*Saccharum officinarum*) now planted in tropical countries contains from 16 to 18 per cent. of cane-sugar. Another gramineous plant (*Sorghum saccharatum*), also used as a source of sugar, is a native of Asia. The sugar-cane, as grown in the United States, yields on an average from 70 to 75 per cent. of juice, containing from 6 to 7 per cent. of sugar. Many other species of grasses contain cane-sugar, thus the maize stems after flowering yield a juice which contains from 7·4 to 9 per cent. of sugar, of which about half consists of cane-sugar. This source of sugar was employed by the ancient inhabitants of Mexico for the production of sugar. Many palms, such as *Caryota urens*, used in Ceylon for the preparation of jaggery, also contain sugar. In Java and many of the East Indian Islands the Arenga palm (*Saguerus sacchifera*) and other species are employed as sugar-bearing plants.

Marggraf[1] was the first to point out that sugar is contained in many kinds of fleshy roots, especially in those of beet (*Beta vulgaris*). These roots usually contain from 7 to 11 and sometimes 14 per cent. of sugar.[2] According, indeed, to Scheibler[3] as high a percentage as 20 is sometimes reached, and tubers containing less than 10 per cent. cannot now, owing to the fiscal arrangements in Germany, be profitably used for the manufacture of beet-root sugar. Cane-sugar also occurs in the roots of *Daucus carota*, *Pastinaca sativa*, *Sium sisarum*, and others. Madder-root likewise contains from 14 to 15 per cent. of sugar.[4] It is moreover found in many seeds, such as almonds, walnuts, hazelnuts, and barley. Coffee-beans, before roasting, contain from 6 to 7 per cent.[5] The sap of many trees is also rich in sugar, as, for example, that of the lime, birch, sycamore, and especially the maple, the sugar-maple (*Acer saccharinum*) having long been used as a source of sugar in the Northern States. Cane-sugar is likewise found in the juice of many fruits, but almost always accompanied by invert-sugar (p. 494). As this latter sugar is derived from cane-sugar by the action of

[1] Schriften, *Berlin Acad.* 1747.
[2] Gmelin, *Handbook Organ. Chem.* xv. 239.
[3] *Ber. Entw. Deutsch. Chem. Ind.* ii. 186.
[4] Stein, *Journ. Prakt. Chem.* cvii. 444.
[5] Graham, Stenhouse, and Campbell, *Quart. Journ. Chem. Soc.* ix. 33.

acids and of certain ferments, it has generally been supposed that cane-sugar is first formed during the process of ripening, and that this is afterwards converted into invert-sugar. Much may, however, be said against this view. Thus in acid fruits, such as the orange, the quantity of cane-sugar regularly increases during the ripening,[1] and the most acid of all fruits, the lemon, contains to 1 per cent. of invert-, 0·4 per cent. of cane-sugar, whilst grapes and sweet cherries do not contain any cane-sugar, though it is present in quantity in the juice of pine-apples and St. John's bread. In other instances it has been shown that the formation of invert-sugar precedes that of cane-sugar. Thus the saccharine juice formed during the early period of vegetation contains only invert-sugar,[2] and this appears to be the case with the sugar cane itself, as the cane when covered with young green leaves contains considerable quantities of invert-sugar, which passes into cane-sugar when the leaves dry up.[3]

The nectar of flowers contains cane-sugar; in that of the flowers of *Rhododendron ponticum* it may even be found in crystals,[4] and in the nectar from a single flower of *Cactus ackermanni*, Braconnot found 0·1 grm. of sugar.[5] In most cases invert-sugar accompanies the cane-sugar.

The quantity of sugar contained in the nectar of certain flowers has been determined by A. S. Wilson,[6] who finds that in order to produce 1 kilo. of sugar 5,600,000 flowers of red clover must be used.

Honey is likewise a mixture in varying proportions of the two sugars, as it is obtained by the bees from the nectar. If bees be fed with grape-sugar their honey contains this variety of sugar.[7] Röders found that heather-fed honey contained invert- but no cane-sugar, whilst Cuba honey contained none of the latter, but consisted chiefly of dextrose.

## SUGAR MANUFACTURE.

**818** From crude beginnings, the manufacture of sugar has attained gigantic proportions and a marvellous degree of completeness, due to a fertile union of both chemical and engineering science.

[1] Berthelot and Buignet, *Compt. Rend.* li. 1094.
[2] Jackson, *ib.* xlvi. 55; Leplay, *ib.* xlvi. 444.
[3] Icery, *Ann. Chim. Phys.* [4], v. 350.
[4] Stammer, *Jahresb.* 1849, 464.
[5] *Berzel, Jahresb.* xxiv. 454.
[6] *Pharm. Journ. Trans.* [3], ix. 225.
[7] Röders, *Jahresb.* 1863, 574.

The simplest process for obtaining sugar is that from the sugar-cane, which still yields the largest quantity of this invaluable article. The juice of the cane contains about 24 per cent. of sugar, about 1·7 per cent. of inorganic salts, and about 0·2 per cent. of organic acids, albuminous matter, &c. Only about half this amount is, however, obtained in practice in the form of crystallizable sugar.

The various causes which bring about a considerable loss are mainly the following: In the first place, the hard silicious stem of the cane renders the complete extraction of the juice in the rolling-mill impossible where the cane is crushed by passing between horizontal rollers. These are now commonly heated by steam for the purpose of assisting the outflow of juice, and also because the megasse, as cane after crushing is termed, holds back less juice when crushed hot than when crushed cold. Secondly, the juice is liable to undergo deleterious fermentive change at the temperature of the hot countries where it is made, and in order to avoid loss from this cause, it becomes necessary to work as quickly as possible, and this is done by running the juice directly from the mill through a double metallic sieve (for the purpose of removing most of the suspended matter) into a copper cauldron of 4,000 gallons capacity, called the clarifier. This is heated by a fire placed beneath, and as soon as the juice has reached the temperature of 130° Fahr., cream of lime is added in the proportion of about 4 oz. of quicklime to the gallon of juice, which is enough to cause the formation of a thick scum as soon as the juice boils. This not only takes out of solution the albuminoid and other bodies, the presence of which is liable to cause fermentation, but it also neutralizes the malic and other acids contained in the juice, which if allowed to remain would prevent a portion of the sugar from crystallizing. The clarified juice is then run into a second pan placed alongside the first, and here another scum is formed, which is ladled back into pan No. 1. From the second pan the juice is passed into smaller pans, and in the last one it is still further evaporated until the point of crystallization is reached. This is judged of by the finger-test, that is, a drop of the syrup is placed between finger and thumb, when it must be capable of being drawn out in a stringy mass. This thread of sugar is the longer the more concentrated is the syrup, and when it has a length of 3 cm. the liquor has been sufficiently boiled. The last

scum, which contains a considerable quantity of sugar, and the ash left after burning the megasse, are employed as manure. In former times, deep cast-iron pans were employed, now flat copper pans are used, and these are ranged one above the other so that the juice runs from the first to the last pan by gravitation instead of being ladled out.

The experience gained in the preparation of sugar from beet-root and the improvements which have been made in these processes have done much to improve the cane-sugar manufacture. In the first place, evaporation over an open fire, by which great risk is run of burning the sugar, has been modified by the introduction of heating by steam. This is effected by a coil of pipes placed in a pan, through which high-pressure steam is

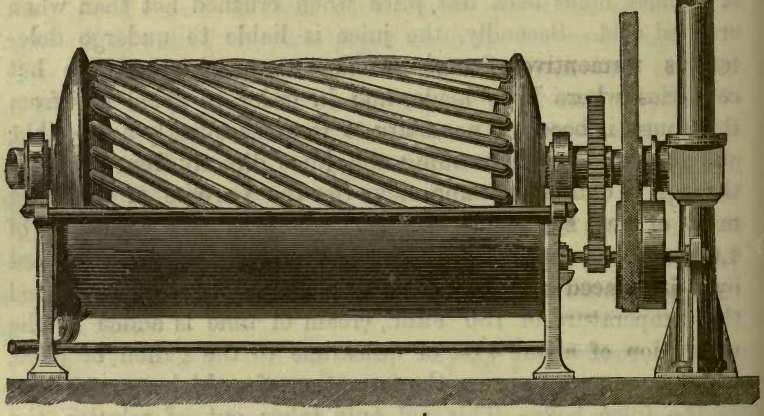


Fig. 122.

passed. But in this arrangement a deposit of lime-salts is apt to form on the steam-pipes, and, in consequence, an evaporator, known as Wetzel's pan, is now much used. The construction of this is shown in Fig. 122. The steam passes through a system of pipes moving on a horizontal axis, and the sugar juice, placed in the lower pan, is carried in a thin film over the heated surface.

819 Another process for evaporating the raw juice, also largely used in the colonies, is carried out by help of an arrangement known as the concretor of Mr. Alfred Fryer, an elevation of which is shown in Fig. 123 and a plan in Fig. 124. In this, the clarified juice is very quickly evaporated but not burnt. The

object of this process, to use the words of the inventor, is to

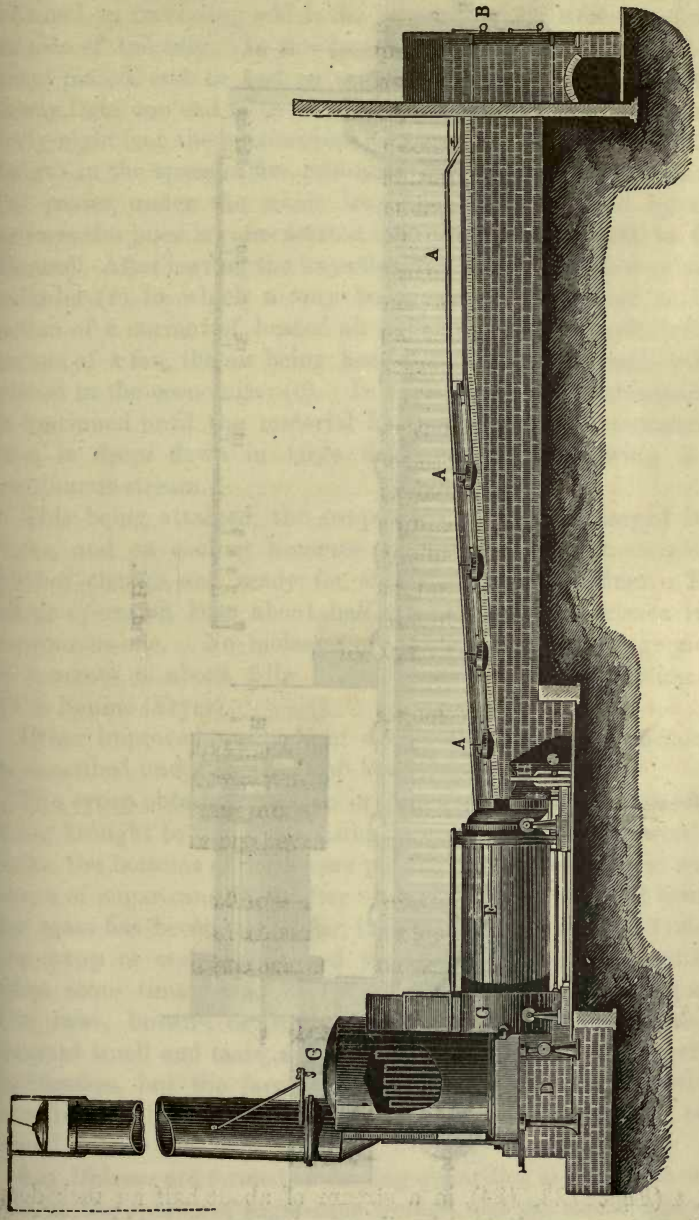



Fig. 123.

turn the juice at once into a solid mass which can easily be packed and is not subject to loss by drainage. To accomplish

this, the clarified juice is first run over a series of shallow trays,

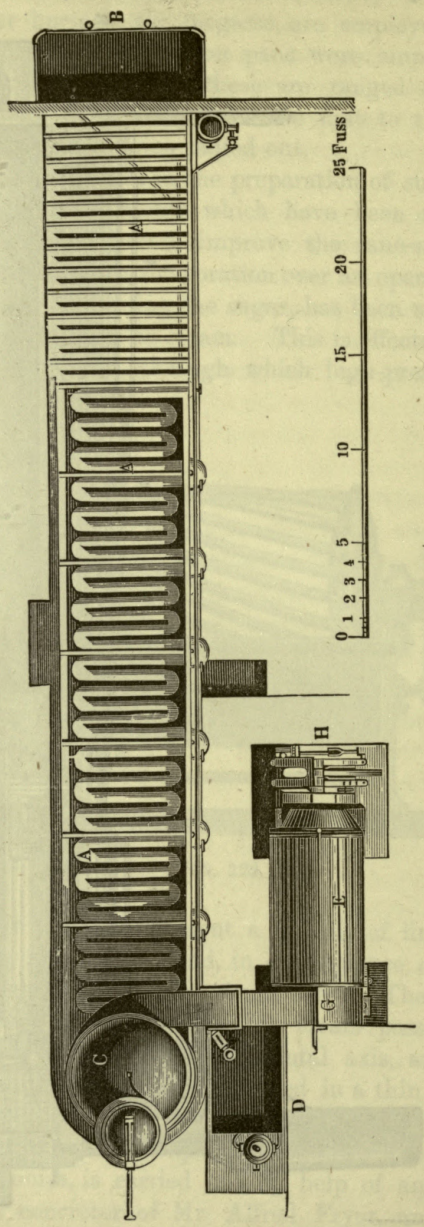



FIG. 124.

A A (Figs. 123, 124), in a stream of about half an inch deep. These trays are divided by ribs running from one side nearly to

the other, so that each tray forms a continuous narrow serpentine channel, in traversing which the juice passes six times from side to side of the tray. In the large sizes there are ten of these trays placed end to end, so arranged that the juice can flow freely from one end to the other of the series, or on a length of forty-eight feet, the juice traversing, therefore, about six times this length in the space of five minutes. The flame from the furnace (B) passes under the whole length of the trays, and by this process the juice is concentrated to a density of from 30° to 40°, Baumé. After leaving the trays the juice passes into the revolving cylinder (F), in which a very large surface is exposed to the action of a current of heated air drawn through the cylinder by means of a fan, the air being heated by passing through tubes placed in the economizer (C). In this cylinder the concentration is continued until the material has attained such a consistency that it drops down in large flakes instead of flowing in a continuous stream.

This being attained, the evaporated mass is discharged into casks, and on cooling becomes solid, incapable of undergoing further change, and ready for shipment to the refiner. The whole operation lasts about half an hour, and the process is a continuous one. No molasses are made, and the average yield of concrete is about 2 lbs. to the gallon of juice standing at 10°·5 Baumé (Fryer).

Other improved methods of evaporating the sugar-juice will be described under the head of Beet-Sugar.

The syrup obtained by one or other of these processes, after being brought to the crystallizing point, is thrown into wooden tanks, the bottoms of which are pierced with holes stopped with pieces of sugar-cane. If, after standing for twenty-four hours, the mass has become granular, it is stirred and the non-crystalline syrup or *molasses* allowed to run off, an operation which takes some time owing to the viscid character of the liquor. The raw-, brown-, or Muscovado-sugar thus obtained has a pleasant smell and taste, and is often used without any further purification, but the largest quantity undergoes the operation of refining; the details of this operation will be given in the sequel.

820 *Molasses* are formed in varying quantities, according to the climate, the species of sugar-cane worked, and the care displayed in the operations. They consist of a mixture of cane-sugar, uncrystallizable sugar, caramel, gum, and salts. Molasses

are used as an article of food, but chiefly employed in the manufacture of rum.

**821** *Beet-root Sugar Manufacture.* The observation first made by Marggraf that beet-roots contain sugar remained without fruit until his pupil, F. K. Achard, corroborating the fact, established in 1769 the first beet-root sugar works in Germany, and this was soon followed by others. This trade received a great impetus owing to Napoleon's decree in 1806 forbidding the import of foreign sugar, which sent up the price of cane-sugar to a very high point, but after the overthrow of the Empire most of the beet-root sugar-works were obliged to close. The experience, however, gained in the few works which were able to hold out, gave rise to such improvements in the processes as to render a subsequent revival of the trade possible. These improvements consisted, first, in better plans for evaporating the juice; secondly, in a method for revivifying the animal charcoal which after a time loses its decolourizing power; and thirdly, in the progress made by agricultural chemistry pointing out the methods by which a root rich in sugar and poor in salts can be grown. The beet-root sugar industry has attained gigantic dimensions in France, Germany, Austria, and Russia. It is also largely and very successfully worked in Belgium, whilst other countries, such as Holland, Sweden, and Italy, also produce beet-root sugar. In England and her colonies this manufacture is not carried on.

In order to obtain the juice of the beet, the roots, cleansed and washed, are rasped by machinery and the liquor extracted by hydraulic presses and the solid mass dried by centrifugal machines. According to the old *maceration process* of Schützenbach the roots were sliced, then dried, and then lixiviated with water at 80° C. This method possesses the advantage of being capable of continuous working throughout the year, but the extraction takes place slowly, and the high temperature needed is apt to bring into solution substances which act prejudicially on the yield of sugar. Hence the same manufacturer afterwards introduced another method by which the roots were systematically lixiviated in a series of tanks in a similar way to that now employed in the extraction of soda in the black-ash process (see Vol. II. Part I. p. 148). This process gave place to another suggested by Dubrunfaut under the name of the *diffusion* process, and introduced on the large scale by Robert. The freshly-sliced roots are systematically

lixiviated as just described, and the liquors dialysed, when the sugar solution passes, together with the other crystalloids, through the cell-walls, whilst the colloidal bodies, such as albumen, gum, &c., remain behind, so that in this way a much purer juice is obtained than by the older processes.

In order to purify the beet-root juice it is first heated to about 85° C., at which temperature the albumen coagulates, and then about 0·5 to 1 per cent. of lime is added in the form of milk. The liquid is next filtered off from the scum by means of a press, and carbon dioxide passed into the liquor in order to decompose the saccharate of lime which is formed. These processes, which are termed *defecation* and *saturation*, are often carried out in one operation. The defecated juice is then mixed with a larger quantity of lime, usually amounting to 5 per cent., and again treated with carbon dioxide, and thus the purification completed. Formerly the addition of so much lime was not made, as it proved impossible to extract the sugar from the large quantity of scum which forms, but this has now been accomplished by the use of improved forms of filter-presses. The above method is chiefly used for the purification of juice obtained by diffusion. After saturation the juice is filtered through a mass of animal charcoal placed in high cylinders, by which not only is the colour removed but with it many impurities. After a time this "char" loses its decolourizing power and it is necessary to *revivify* it by first washing it with water containing a little hydrochloric acid when fermentation takes place. As soon as this is over the char is washed with water, dried, and ignited in closed cylinders.

The filtered and colourless juice is now concentrated by evaporation, an operation which is now universally carried on in *vacuum-pans* under a diminished pressure. Fig. 125 shows the section of a vacuum-pan such as is used for boiling down the juices both of beet- and cane-sugar, fresh juice being added from time to time until the mass begins to "show grain." This crystallization is allowed to continue for a certain time, then air is admitted, and the charge run out into a tank for cooling, when further crystallization occurs. By placing three of these vacuum-pans in series, the steam arising from the first evaporation in pan No. 1 passes through a "save-all" (Fig. 125, H) to catch any juice which primes, into the steam-drum of pan No. 2; and the same operation is repeated with the steam from the juice in pan No. 3. This leads to

considerable economy of fuel as compared with the steam evaporating pans used under the ordinary atmospheric pressure.

**822** *Sugar Refining.* The first process of the sugar refiner, technically termed "melting," consists in dissolving the raw sugar in hot water, or by means of a jet of steam, and, when necessary, precipitating the impurities either by addition of lime, animal charcoal, or albuminous substances. The clarified liquor is then

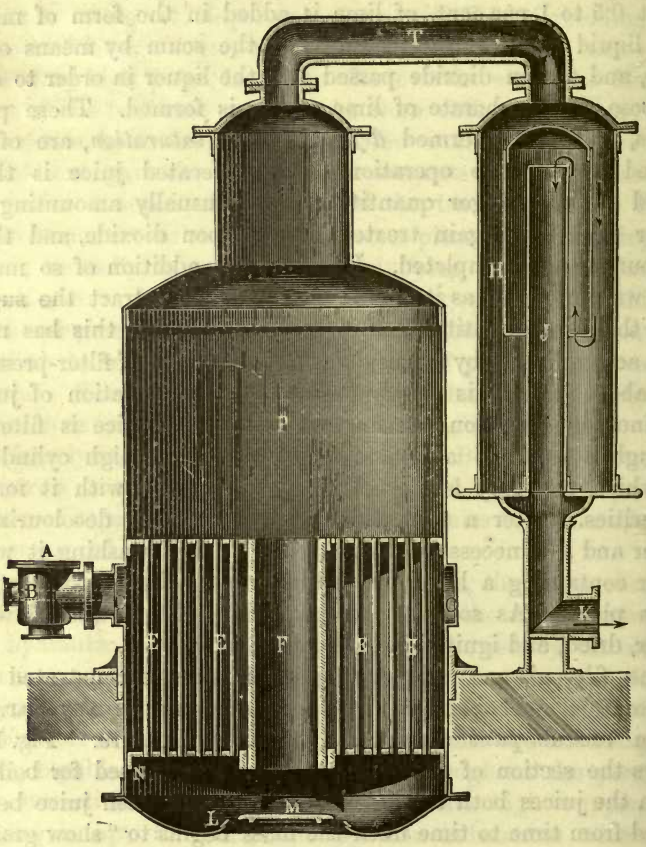



FIG. 125.

filtered through bag-filters, and next flows on to the animal charcoal filters to be decolourized, whence it passes to the vacuum-pans for boiling down.[1] The vacuum-pan of the refiner is a complicated

[1] This decolourizing action of animal charcoal appears not to be due to oxidation from absorbed oxygen, as a sample of char ignited in vacuum with a sprengel, and therefore freed from absorbed oxygen, acted as well as the ordinary char.

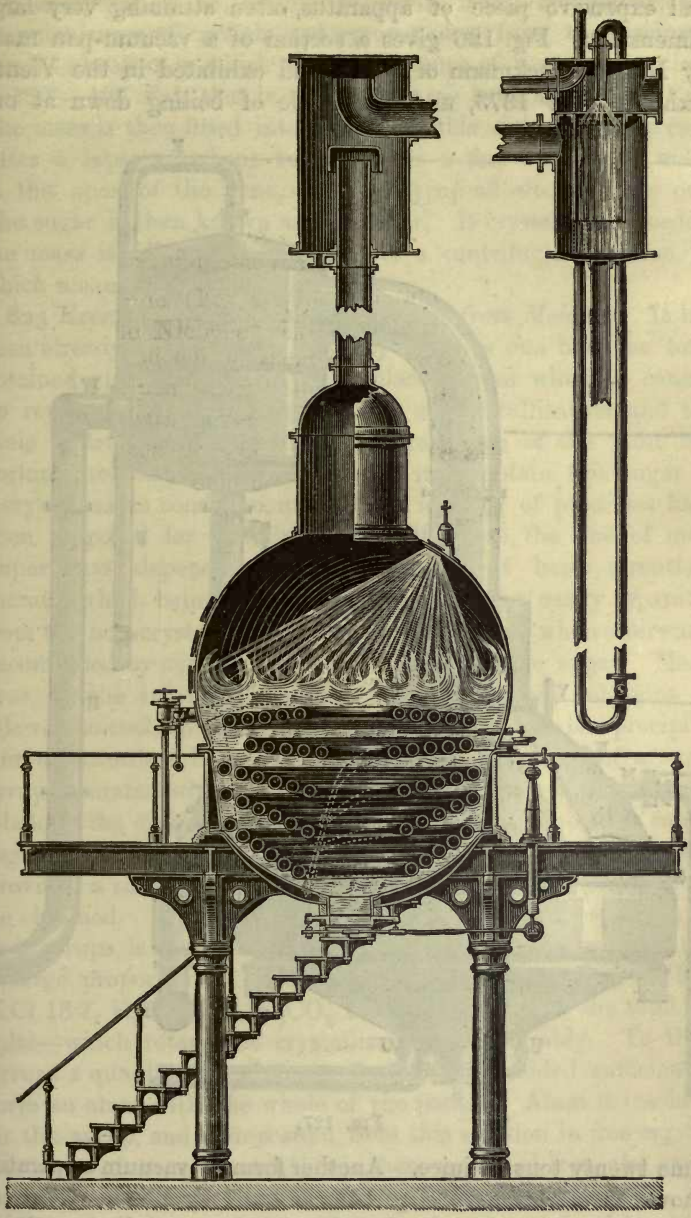


FIG. 126.

and expensive piece of apparatus, often attaining very large dimensions. Fig. 126 gives a section of a vacuum-pan made by Messrs. Heckmann of Berlin and exhibited in the Vienna Exhibition of 1873, and is capable of boiling down at one

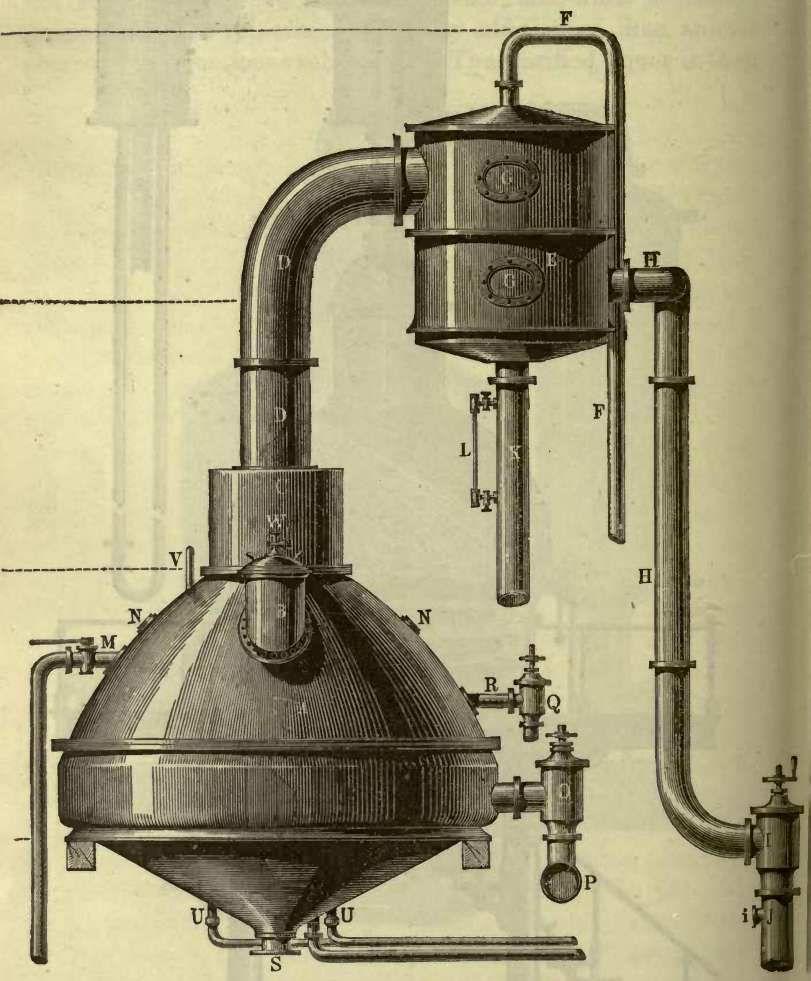



Fig. 127.

time twenty tons of juice. Another form of vacuum apparatus, shown in elevation in Fig. 127, is built by Messrs. Adam, of Greenock, and is drawn to a scale of $\frac{1}{72}$. At each operation it boils twenty-seven tons of juice, and it is from 4 to 4·5 metres in diameter.

The operation of boiling to grain being completed, the granular mass of crystals and syrup passes from the vacuum-pan into heaters in which the temperature of the mass is raised to 180°—190° Fah. that in the pan having been about 150° Fah. The mass is then filled into conical moulds and allowed to cool. After a lapse of about twenty hours a fine opening is made at the apex of the cone, and the syrup allowed to flow out. The sugar is then known as loaf-sugar. If crystals are needed, the mass is filled into the sieve of a centrifugal machine, by which means the syrup is removed.

823 *Extraction of Crystallizable Sugar from Molasses.* It has been already stated that a quantity equal to one half the total obtained sugar remains in the molasses, from which it cannot be removed by simple evaporation or crystallization, and the same is true of the beet-root liquors. One of the most important problems for the sugar-boiler is to obtain this sugar in a crystallizable condition, and a large number of processes have been proposed for effecting this. Of these, the one of most importance depends on the formation of basic strontium sucrate, which being insoluble in syrup can be easily separated from the non-crystalline sugar syrup, and which, when afterwards decomposed by carbonic acid, yields a crystalline sugar. Moreover, if the insoluble sucrate prepared in hot solutions be allowed to cool, the basic compound decomposes with precipitation of strontium hydroxide, the solution consisting of a sugar syrup saturated with this hydroxide. By this means nearly the whole of the crystallizable sugar contained in the molasses can be regained, and the process bids fair to become generally adopted provided a sufficient quantity of native strontianite ($SrCO_3$) can be obtained. A second plan also largely employed, especially for beet syrups, is known as the alum process. These syrups contain a large proportion of potash salts—according to Dr. Wallace, KCl 18·7, $K_2SO_4$ 4·18, $K_2CO_3$, or 53·8 per cent. of the total dry salts—which retard the crystallization considerably. To these syrups a quantity of sulphate of alumina is added sufficient to form an alum with the whole of the potash. Alum is insoluble in the syrup, and is deposited from this solution in fine crystals known as alum meal, and this is then separated from the syrup which is afterwards worked up for crystallizable sugar.

The employment of the *vinasse* for the preparation of potash-salts, methyl-compounds and ammonia, has already been noticed (Vol. III. Part I. page 196).

*Sorghum Sugar.* The manufacture of sugar from this source appeared to offer a large measure of success, inasmuch as this cane thrives in climates too hot for beet-root culture, but too cold for that of the sugar-cane proper. Owing, however, to the fact that this plant yields a larger proportion of invert-sugar than ordinary cane-juice, and likewise contains gum, albumen, and salts in larger quantity, a great extension of this manufacture has not taken place. Recently, however, Stewart has proposed a plan by which crystallizable sugar can be economically prepared from Sorghum cane, and in the south of Russia this plant is said to yield from 14·2 to 16·5 per cent.[1]

*The Extraction of Sugar from plants* on the small scale is best effected as follows: the plant is dried, sliced, and repeatedly extracted with seventy per cent. alcohol. On cooling, the filtered alcoholic solution deposits crystals of sugar, and a further crop is obtained on evaporation (Marggraf). Another plan is to prepare sucrate of lime, or of strontia, from the juice, and to decompose these compounds by carbon dioxide.

## Sugar Analysis.

**824** At the commencement of the beet-root sugar manufacture, the quantity of sugar was estimated by extraction with alcohol by the method already given. Afterwards, this process was superseded by that of allowing the juice to ferment on addition of yeast, the quantity of alcohol and of carbonic acid generated being determined. Another plan was to take the specific gravity of the juice before and after the fermentation, the alcohol being removed by ebullition, and the volume made up to the original one by the addition of water.

These and other methods have now been replaced by that of *optical analysis.* This depends upon the special power which solutions of saccharoses and glucoses possess, of deviating the plane of a ray of polarized light, and upon the law discovered by Biot, that the amount of this deviation to the right or to the left is directly proportional to the weight of sugar contained in the unit volume of liquid, and to the length of column through which the ray passes. This has, however, been found not to be perfectly true, as Hesse[2] and Tollens[3] have shown that the same quantity of sugar possesses a somewhat greater rotatory

[1] *Nature*, vol. xxviii. 376.
[2] *Ann. Chem. Pharm.* clxxvi. 89, 189.
[3] *Ber. Deutsch. Chem. Ges.* xi. 1800.

power in dilute than in concentrated solution. Still this error does not materially affect the practical estimation.

Many different kinds of polariscopes have been, and are now employed in the optical analysis of sugars. One of the simplest forms of saccharimeter, as suggested by Mitscherlich and Soleil, is shown in Figs. 128 and 129 respectively. The two Nichol's prisms[1] are placed at each end (*a* and *b*) of the apparatus, and the liquid to be examined is brought into the tube (Fig. 130), and this then placed between the Nichols in the direction denoted by the dotted line (Fig. 129). If, before the tube is placed in position, the Nichol's prisms are

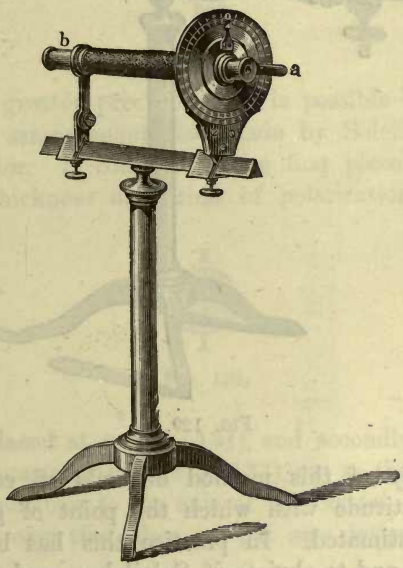



Fig. 128.

so turned that no light passes through, it will be observed that light is seen to pass through the prisms after the tube is placed in position, and the Nichol (*a*) will have to be turned round through a certain angle in order to prevent any light passing. The magnitude of this angle is read off on the divided circle (Fig. 128). The deviation is in this case proportional to the volume-percentage of sugar, as the length of column remains constant. Thus supposing that a sugar solution containing 15 grms. of pure cane-sugar, in 100 cbc. be found to effect a

[1] For a description of this phenomena of polarization, works on Physics must be consulted.

deviation of + 20°, then 10·5 grm. dissolved in 100 cbc. will be found to give a deviation of + 14°, for 20 : 15 : : 14 : 10·5. If fifteen grms. of any sugar-containing substance be dissolved in 100 cbc. of water, and if the angular rotation of this solution be multiplied by five, the percentage by weight of sugar is obtained; thus a solution of fifteen grms. of raw sugar gave a rotation of 19°, or the sample contains $19 \times 5 = 95$ per cent. of cane-sugar.

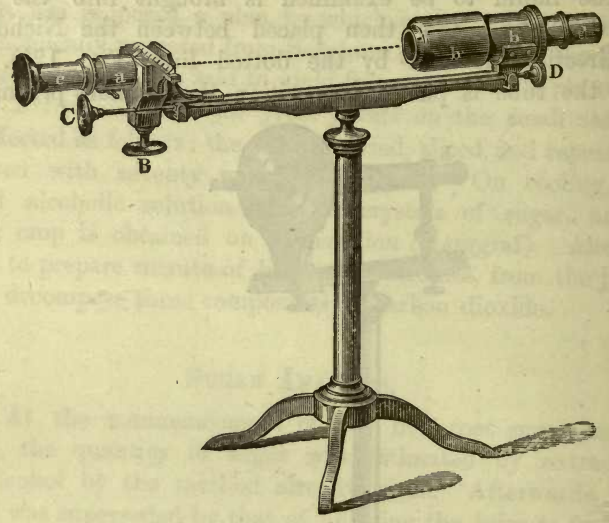



Fig. 129.

The accuracy of this method depends of course on the degree of exactitude with which the point of greatest darkness can be estimated. In practice this has been found to be a difficulty, and to obviate it, Soleil has made the following addition to the polariscope. In front of the prism (*b*) Fig. 131 is placed a plate of rock-crystal, 3·75 or 7·5 mm. in thickness, and cut at right angles to the axis. This consists of two halves

Fig. 130.

(Fig. 132), one of which (*g*), turns the plane to the right, and the other (*d*), possesses the opposite or laevo-rotatory power. Now when the prism (*a*) is rotated, each half of the quartz plate will attain different tints, and the same effect will be observed if,

instead of rotating the prism, the tube containing a solution of sugar be placed between the prisms. In order to bring about an identity of tint in the halves of the quartz plate, the prism (*a*) must be turned through a given angle. The same object is

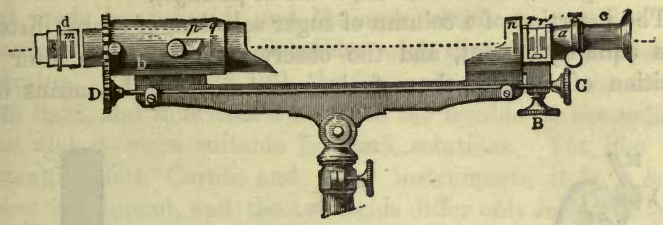



Fig. 131.

attained with greater precision than is possible by turning the prism, by an arrangement also made by Soleil, and termed the compensator. It consists in the first place of a plate of quartz (the thickness and kind of polarization of which is

Fig. 132.

immaterial), placed at *n* (Fig. 131), and secondly of two equal right-angled quartz prisms (Fig. 133), cut so that the surfaces *f f* are perpendicular to the axis of the crystal. These prisms can slide one over the other, so that any desired thickness of

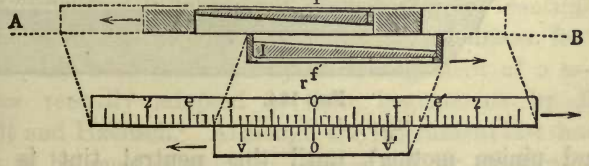



Fig. 133.

quartz can be brought in the line of vision. A scale and vernier attached to these quartz prisms are so arranged that when the vernier points to 0°, the thickness of the two prisms is equal to the thickness of the plate *n*, so that, possessing opposite rotatory

powers, the optical action of the one is counterbalanced by that of the other. If, when thus arranged, a source of light be allowed to pass through the apparatus into the eye, the two halves (*g d*), of the quartz plate will appear of a violet colour, (neutral point, transition tint, *teinte de passage*).

The insertion of a column of sugar solution, of course disturbs this equality of tint, and the observer has then to alter the position of one or other of the quartz prisms (by means of a

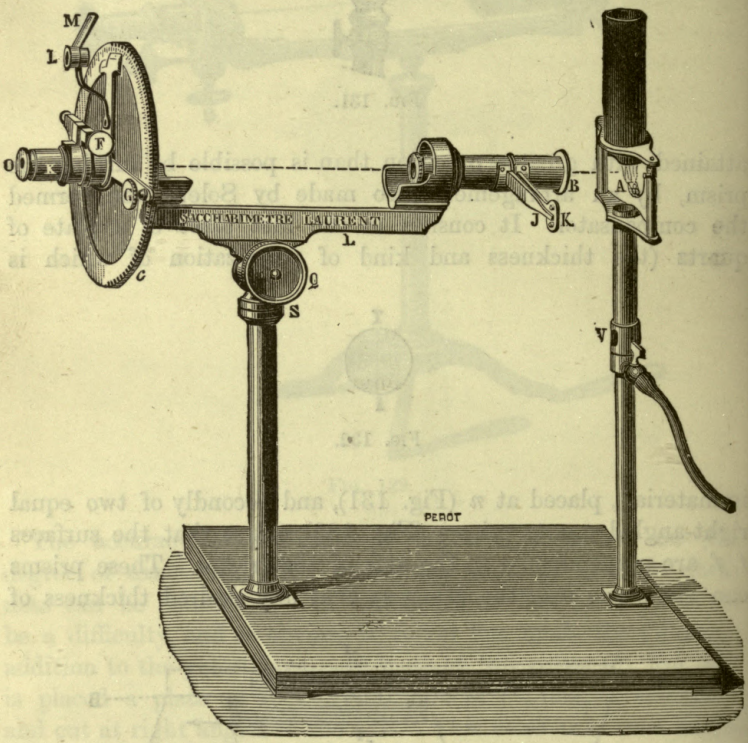



FIG. 134.

rack and pinion motion), until this neutral tint is again reached.

**825** Many other forms of saccharimeters are employed; of those in general use may be mentioned, (1) the Laurent *pénombre*, or half-shadow instrument (Fig. 134), (2) the Soleil-Ventzke saccharimeter, (3) Wild's polaristrobometer (Fig. 136), and (4) the form of apparatus now generally adopted both in England

and Germany, manufactured by Messrs. Schmidt and Haensch of Berlin (Fig. 135).

For the exact description of these different instruments we must refer the reader to Landolt's *Handbook of the Polariscope* (Macmillan & Co., 1882). Suffice it here to say that the instrument made by Schmidt and Haensch, claims to combine the advantages of the Soleil-Scheibler with those of the Laurent apparatus. In common with the former it admits of the use of white light, and thus does away with the trouble of the sodium flame, and is more suitable for dark solutions. Yet, like the Laurent, Jellett, Cornu, and other instruments, it is a *half-shadow* instrument, and the two fields differ only in intensity of light and not in colour (Jellett), so that the personal error is less than when the transition tint has to be reached.

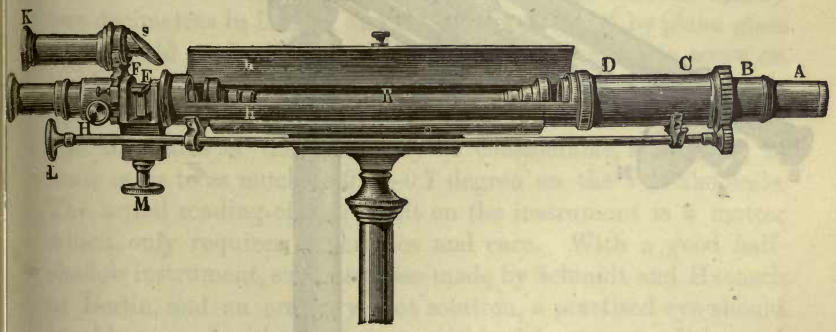



FIG. 135.

The one disadvantage attending the use of this instrument, viz. that the chromatic dispersion due to the rotatory power of sugar solutions and quartz are not absolutely identical, and that therefore the field is not perfectly colourless for large rotations, has been remedied by an arrangement of a so-called regulator recently adapted to their instruments by Messrs. Schmidt and Haensch.[1] Although the instrument last described is that to be most strongly recommended for practical sugar-work, there is no doubt that for more strictly scientific purposes the Laurent instrument with sodium flame, is for many reasons the most accurate.[2]

[1] See Landolt, *Polariscope*, p. 155, and also *Zeitschrift des Vereins für die Rübenzucker Industrie*, Sept. 1881, and Jan. and Dec. 1880.

[2] Gamgee, *Phys. Chem.* pp. 9 and 10.

826 The following is a short description of the method adopted in the optical analysis of a cane-sugar contained in a solution of beet-root sugar, which it may be assumed does not contain any appreciable quantity of glucose, the instrument used being a Soleil-Ventzke, 1° on the scale corresponding to 0·26048 grms. of sugar in 100 cbc. of water.

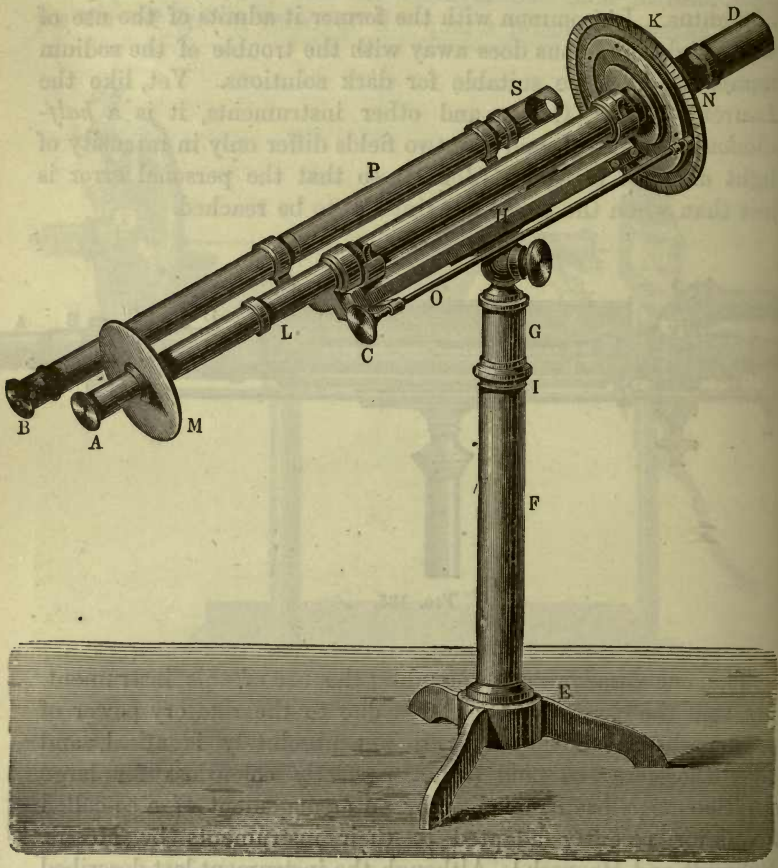



FIG. 136.

The *modus operandi* is as follows :

26·048 grms. (in case of a Ventzke instrument), of the sample which has been thoroughly mixed in a mortar, are weighed out into a German-silver dish of a convenient size and shape. From this the sugar is washed with as little water as possible into a 100 cbc. flask, exactly graduated.

As soon as the sugar is all dissolved, a few cbc. of a solution of basic acetate of lead (the amount varies with the nature of the sugar) are added, and about 2 cbc. of well washed $Al_2(OH)_6$ in water; the former solution precipitates a great part of the colouring matter present, and the alumina prevents any of the very finely divided lead precipitate from passing through the filter, and thus a clear and bright filtrate is obtained.

The volume occupied by the lead precipitate and of the alumina has been proved to be insufficient in most cases to affect the true polariscope reading.

The use of animal charcoal for preparing a sugar solution for the polariscope is now quite given up, owing to the fact that it absorbs some of the sugar from solution, and hence too low a reading is obtained.

The clear filtrate is now poured into a glass tube of exactly two decimetres in length, and the two ends closed by plane glass covers held on by brass heads, care being taken not to screw on the heads so tightly as to exert more than a very gentle pressure upon the cover-glasses, otherwise the error introduced by rotation due to strains of the glass may be considerable, amounting in some cases to as much as 0·5—0·7 degree on the Ventzke scale. The actual reading of the result on the instrument is a matter which only requires experience and care. With a good half-shadow instrument, such as those made by Schmidt and Haensch of Berlin, and an ordinary beet solution, a practised eye should be able to read with certainty to within 0·1 per cent. It is usual to take several readings, which should not differ by more than 0·2, the mean being taken as correct. It is also well each time, before using the instrument, to check the zero point of the scale. This is not so important however, with the half-shadow instruments in which a monochromatic flame is used, for in this case the zero point can only be affected by some slight displacement of some essential portion of the instrument, whereas in the case of the older colour instruments, and of those instruments using a white light, a mere change in the gas-pressure was sufficient to upset the zero.

The percentage of cane-sugar thus found by direct reading, is taken for trade purposes to be the true representation of the amount of cane-sugar present, and all transactions in the English and Scotch markets are based on this assumption. Doubtless in many cases the results are sufficiently correct, but that they cannot be so in all cases will be seen from the following list of

other active substances than sugar that are found in beet-roots, and many of which find their way into the raw sugars :—

| | |
|---|---|
| Malic Acid . . . . | Laevo-rotatory. |
| Asparagin and Aspartic Acid. | Both + in acid and − in alkaline solution. |
| Glutamic Acid . . . | +. |
| Invert sugar . . . . | −. |
| Beet-gum . . . . | −. |
| Dextrin . . . . | + very strongly. |

827 *Estimation of Soluble Ash.* The compounds of alkali and other metals, which occur in the sugar with various organic and inorganic acids, are known as soluble ash. The importance of ascertaining the total quantity of these constituents is indicated by the fact that they influence to a great degree the amount of crystallizable sugar which can be obtained, inasmuch as they prevent the crystallization of a considerable quantity of the cane-sugar. In practice it is found that 1 per cent. of soluble ash prevents 5 per cent. of sugar from crystallizing. For this determination, about 2 grms. of sugar is placed in a tarred platinum dish, and moistened with pure concentrated sulphuric acid, then charred carefully, and ignited in a platinum muffle until the whole of the organic matter is destroyed. It is the custom in the trade to deduct $\frac{1}{10}$ of the weight of ash as roughly representing the increase in weight due to the replacement of the various acids by sulphuric, and the difference multiplied by five is deducted from the percentage of sugar obtained by the saccharimeter.

These determinations are the only ones needed in the case of high class beet-root sugars. In certain cases, however, of low-class samples, the amount of insoluble ash (silica, &c.), is determined, and this deducted from the weight of soluble ash. The quantity of water in beet-sugar is also sometimes determined as a check, but it does not enter into the calculation of the net value. The following example shows the result of an analysis of beet-sugar:

Cane-sugar (found by polariscope) = 95·40 p.c.
Sulphated ash = 0·0230 less $\frac{1}{0}$ + 0·0207 grms. = 1·03 p.c. from 2 grms. sugar

Percentage of net available sugar, 95·4 − (1·03 × 5) = 90·25.

Such a sugar would probably contain about three per cent. of moisture, and 0·5 per cent. of organic matter not sugar.

828 *Analysis of Cane-Sugars, Jaggery, &c. Estimation of Cane-Sugar and Glucose.* In this case the amount of glucose or invert-sugar present has to be estimated as well as that of the cane-sugar. For this purpose the cane-sugar is estimated optically, as already described. The invert-sugar is estimated by *Fehling's method.* This depends on the fact that an alkaline cupric solution is reduced by glucose, the point at which decolorization of the standard solution occurs being ascertained. In some cases the weight of reduced cuprous oxide is ascertained, but in general the simpler volumetric process is adopted.

The following is one of the best receipts for preparing Fehling's solution:

(*a*) Dissolve 34·639 grms. of crystallized copper sulphate, powdered and dried between filter-paper, in 200 cbc. of hot water.

(*b*) Dissolve in another vessel 173 grms. of pure crystallized Rochelle salt in 480 cbc. of pure solution of sodium hydrate of sp. gr. 1·14.

Add the first solution to the second, and dilute the clear deep blue liquid to 1,000 cbc. and pour into a stoppered bottle of dark blue glass. In such a bottle the solution will keep for a considerable time without decomposing, even though it has not been boiled, as some authors recommend.

The solution is standardized by means of a weak solution of invert-sugar, 2·375 grms. dry powdered cane-sugar are dissolved in a little water and heated for a few minutes to 60° C. with a few drops of concentrated sulphuric acid. The solution is then cooled, neutralized with sodium carbonate, and made up to 500 cbc. Each 10 cbc. of this solution contains 0·05 grm. of invert-sugar, and should be capable of exactly reducing 10 cbc. of the copper solution.

It is usual to take 10 cbc. of the Fehling solution in a small flask, or large test-tube, dilute with 20 cbc. of water, boil and titrate with the sugar solution, boiling again after each addition of the reducing agent. The end of the reaction is indicated by a transition of the colour of the solution from a pale blue to a brown colour. The point may also be confirmed by filtering off a few drops and testing with an acetic acid solution of potassium ferrocyanide.

In the analysis of raw sugars containing glucose the following method is adopted: Of the solution of 26·048 grms. of the sugar in 100 cbc., which has been used for polarizing, 25 cbc. are taken, a slight excess of sulphurous acid is added to remove the lead,

and a little precipitated alumina; the whole is then made up to 50 or 100 cbc. according to the nature of the sugar (it being always desirable to have a solution of such a strength that 10 cbc. contains somewhat about 0·05 grm. glucose). The solution is filtered and 10 cbc. of Fehling titrated by it. From the number of cbc. used the amount of glucose present can easily be calculated. It is in this case supposed that 1 per cent. of soluble ash entails a loss of 5 per cent. of sugar. But the glucose present also acts in a similar way, 1 per cent. of this substance being considered to prevent 1 per cent. of cane-sugar from crystallizing. We thus have the net value of such a cane-jaggery estimated as follows:

Cane-sugar by direct reading of polariscope = 76·80
Glucose by Fehling's test ... ... ... 9·04

Sol. ash = 2 27 p.c. × 5 + 11·35 + 9·04 = 20·39

Net = 76·8 − 20·39 = 56·41 p.c. crystallizable sugar.

The presence of uncrystallizable sugars does not interfere with the results of optical analysis, as they are optically inactive.[1] On the other hand the organic acids and other bodies which occur in the juice are some of them dextro- and others laevo-rotatory. In addition, beet-root molasses contains *raffinose*, $2C_9H_{16}O_8 + 5H_2O$, a tasteless crystalline body which possesses a more powerful dextro-rotatory power than cane-sugar.[2] Practically it appears that the error due to the rotatory power of these substances has been found to lie as often in one direction as the other, and in few cases it exceeds 1 to 2 per cent. For the purpose of checking this reading, the inversion method suggested by Clerget is the best.[3]

*Adulterations.* The above methods are sufficient to determine the value of unadulterated beet- or raw cane-sugar, but if, as has happened in some cases, the sugar be purposely mixed with cheap commercial glucose or maltose, a further examination is necessary. For this purpose advantage is taken of the fact that freshly prepared solutions of dextro-glucose, the principal constituent of commercial glucose, when allowed to stand for some hours, or when gently warmed, lose their rotatory power. Thus a sugar adulterated with 10 per cent. of a solid commercial glucose (and it would not be worth while to add less), will show

[1] Girarde and Laborde, *Comptes Rendus*, lxxxii. 214. 417.
[2] Loisseau, *Bull. Soc. Chim.* xxvi. 335.
[3] Landolt, *Polariscope*, 187, &c.

a difference of from 3° to 4° on the Ventzke scale between the first and second readings, the usual proportion of 26·048 grms. in 100 cbc. being taken.

For other methods of testing for and determining the amount of this adulteration we may refer to Tucker's *Manual of Sugar Analysis*, p. 287.

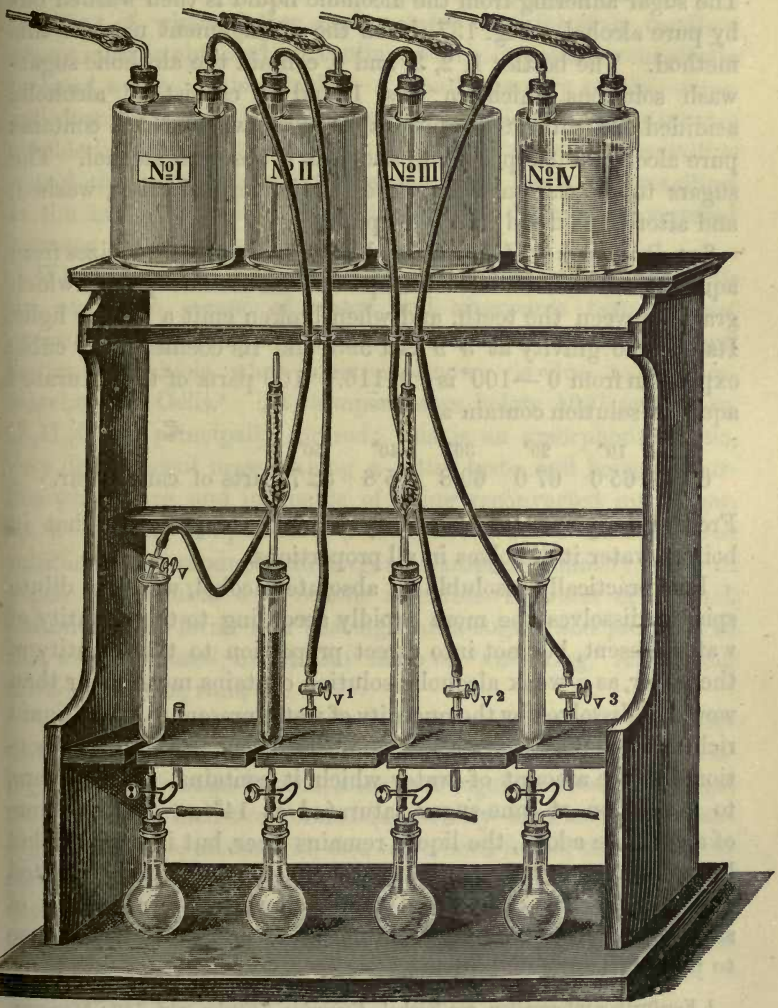



Fig. 137.

829 *Payen-Scheibler's Method.* A totally different method of estimating the quantity of crystallizable sugar in raw cane-

sugar is that proposed by Payen and modified by Scheibler. This process depends upon the fact that if raw sugars be treated with an alcoholic saturated solution of cane-sugar acidified with acetic acid, the colouring matter and other impurities, together with the syrup and other uncrystallizable constituents, are removed, whilst the crystalline sugar remains unchanged. The sugar adhering from the alcoholic liquid is then washed out by pure alcohol. Fig. 137 shows the arrangement used in this method. The bottles 1, 2, 3, and 4, contain the alcoholic sugar-wash solutions which, in Nos. 1 and 2, consist of alcoholic acidified and saturated solutions of sugar, whilst No. 3 contains pure alcohol of 85 per cent., and No. 4 absolute alcohol. The sugars to be examined are placed in the vertical tubes, washed, and afterwards dried in a filter pump.[1]

830 *Properties of Cane Sugar.* Pure cane-sugar crystallizes from aqueous solution in hard transparent monoclinic prisms which grate between the teeth, and when broken emit a bluish light. Its specific gravity at 3°·9 is 1·593, and its coefficient of cubic expansion from 0°—100° is 0·01116.[2] 100 parts of the saturated aqueous solution contain at

| 0° | 10° | 20° | 30° | 40° | 50° | |
|---|---|---|---|---|---|---|
| 65·0 | 65·6 | 67·0 | 69·8 | 75·8 | 82·7 | parts of cane-sugar. |

From this point the solubility increases rapidly, so that in boiling water it dissolves in all proportions.

It is practically insoluble in absolute alcohol, whilst in dilute spirit it dissolves the more rapidly according to the quantity of water present, but not into direct proportion to the quantity of the latter, as a weak alcoholic solution contains more sugar than would be dissolved by the quantity of water present, whilst a liquid rich in alcohol dissolves a less quantity of sugar than is proportional to the amount of water which it contains. If, therefore, to a solution of cane-sugar saturated at 14° an equal volume of alcohol be added, the liquid remains clear, but if more alcohol be added, sugar separates out. Scheibler, who has investigated this subject, has constructed tables showing the solubility of sugar in alcohol of different strengths, a subject of importance to manufacturers of liqueurs.[3]

[1] For further information, see Nichol, *Fresenius Zeitschr.* xiv. 180; Stammer, *Lehrbuch der Zuckerfabrikation;* R. Frühling and J. Schulz, *Untersuchungen v. Zucker and Rohstoffe, &c.* (Vieweg, 1881); Lippmann, *Die Zuckerarten;* Walkoff, *Prakt. Rüben Zuckerfabrikation,* &c.

[2] Joule and Playfair, *Chem. Soc. Journ.* I., 130.

[3] *Ber. Deutsch. Chem. Ges.* v. 343.

Cane-sugar melts at 160°—161° and on cooling does not again crystallize.[1] If kept for some time at a temperature somewhat above its melting-point, it becomes transformed without loss of weight into a mixture of equal molecules of grape sugar, $C_6H_{12}O_6$, and laevulosan, $C_6H_{10}O_5$ (p. 547).[2] If, however, sugar be melted in presence of a small quantity of water, as is done in the manufacture of bonbons and barley-sugar (in the preparation of which latter barley-water was formerly used), a glassy mass is obtained on cooling, which contains mechanically inclosed water. This dissolves a small quantity of the sugar, and deposits it again in the crystalline condition, as a body is more soluble in water in the amorphous state than when crystalline —and this goes on until the whole mass becomes crystalline. If the mass be broken the water can be distinctly recognized between the crystals.[3]

When sugar is heated above its melting point it swells up, owing to escape of water, and afterwards turns brown, *caramel* being formed. This latter is a mixture of several bodies, of which what little is known is due to the researches of Gélis.[4] At temperatures below 190° *caramelan*, $C_{12}H_{18}O_9$, is principally formed; this is an amorphous, brittle, very deliquescent mass, having a bitter taste, and being colourless when pure, and incapable of being reconverted into sugar. At a higher temperature (about 210°—220°) dark-coloured substances are produced in larger or smaller quantity, some of which are soluble and others insoluble in water or alcohol. Caramel is also formed on heating starch-sugar; and prepared in this way it is used, under the name of "colouring," for tinting artificial cognac, rum, &c.

When sugar is more strongly heated certain peculiar aromatic-smelling products are given off, and a residue of porous glistening charcoal remains behind, known as sugar-charcoal. Amongst the products which are formed in the dry distillation of cane-sugar, aldehyde, acetic acid, &c., have been found, together with carbon dioxide, carbon monoxide, and some marsh gas.[5] If sugar be distilled with quick-lime, acetic acid, acetone metacetone, $C_6H_{10}O$,[6] and phorone, $C_9H_{14}O$ (Vol. III. part I. p. 572) are

[1] Berzelius, *Pogg. Ann.* xlvii. 321.
[2] Gélis, *Compt. Rend.* xlviii. 1062.
[3] Mitscherlich, *Pogg. Ann.* lv. 223.
[4] *Ann. Chim. Phys.* [3], lii. 260; lxv. 496.
[5] Völckel, *Ann. Chem. Pharm.* lxxxv. 59; Kaiser, *Jahresb.* 1862, 472.
[6] Gottlieb, *Ann. Chem. Pharm.* lii. 127; Schwarz, *ib.* lxxvi. 292.

formed,[1] and amongst the gases evolved, acetylene and its homologues occur.[2] Metacetone is a pleasantly-smelling liquid which boils at 84°, and is oxidized by chromic acid solution to carbon dioxide, and acetic and propionic acids.

Dry sugar is carbonized by concentrated sulphuric acid only on warming, whilst a concentrated syrupy solution is acted on in the cold; the sugar blackens and swells up enormously, carbon monoxide, carbon dioxide, and sulphur dioxide are evolved, and charcoal remains behind. On heating with strong hydrochloric acid a similar action occurs.

When sugar is boiled with pure water it does not undergo change; in the presence of acids, however, it is transformed into invert-sugar (p. 545). This inversion is effected even by carbonic acid, taking place very slowly in the cold, as is the case also when other dilute acids are employed. If, however, a larger solution saturated with carbon dioxide be heated in a closed tube for a few hours to 100° the conversion is at once completed.[3]

When sugar is heated with water to 160° it is decomposed with formation of formic acid, carbon dioxide, and charcoal.[4] At a temperature of 280° the two last-named products are formed together with some pyrocatechin, $C_6H_6O_2$, a derivative of benzene, $C_6H_6$.[5]

Cane-sugar is not carbonized when heated with caustic potash solution, and does not precipitate cuprous oxide from an alkaline copper solution. If, however, to an ammoniacal silver solution cane-sugar be added, and then some caustic soda, a mirror-like deposition of silver takes place on warming.[6]

If sugar be triturated with eight parts of lead oxide the mixture takes fire. When fused with caustic potash it yields formic acid, acetic acid, propionic acid, oxalic acid, acetone and metacetone (Gottlieb).

When yeast is added to a solution of cane-sugar no immediate fermentation is produced, but this takes place on standing, as invert-sugar is then formed, and this is then acted upon by the ferment. Sugar acts as an anti-putrescent, and is therefore used in the preservation of fruit.

831 *Metallic Compounds of Sugar.* Cane-sugar combines with

[1] Benedict, *Ann. Chem. Pharm* clxii. 304.
[2] Berthelot, *Jahresb.* 1858, 220.
[3] Von Lippmann, *Ber. Deutsch. Chem. Ges.* xiii. 1822.
[4] Loew, *Zeitsch. Chem.* 1867, 510.
[5] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* iv. 15.
[6] Salkowski, Hoppe-Seyler's *Zeitsch. Phys. Chem.* iv. 133.

various oxides and hydroxides, forming compounds the exact constitution of which has not as yet been determined. These compounds are probably formed by the replacement of hydrogen in hydroxyl by the metal, and they have usually been termed saccharates, but as this name is also used to designate the salts of saccharic acid, it is, therefore, convenient to adopt for the compounds at present under consideration the French term of *sucrates*.

*Sodium Sucrate*, $C_{12}H_{21}NaO_{11}$, separates as a semi-fluid mass on the addition of a concentrated solution of caustic soda to a solution of sugar in alcohol; the reaction is accompanied by an evolution of heat. After washing with alcohol and drying in an atmosphere of carbon dioxide it forms a translucent friable mass, possessing a strongly alkaline taste, and dissolving readily in water. The solution is decomposed by carbon dioxide, sugar being again formed.[1]

The corresponding potassium exhibits exactly analogous reactions.

*Ammonium Sucrate*, $C_{12}H_{21}(NH_4)O_{11}$. Sugar absorbs dry ammonia, and is transformed into a viscous mass which contains 4·72 per cent. of ammonia, this corresponding to the above formula. On exposure to air the ammonia escapes, and sugar is left behind.[2]

*Sucrates of Calcium.* At the close of the last century, Löwitz noticed the fact that lime dissolves readily in an aqueous sugar solution, the amount of lime dissolved depending upon the strength of the sugar solution,[3] and also upon the temperature,[4] being the greater the more sugar is present, but diminishing with the increase in temperature of the liquid. This fact being explained by the behaviour of the sucrates as described below.

This solution, which has an alkaline and bitter taste, may be used instead of soda solution in volumetric analysis (Peligot), and it is also used in medicine. The *liquor calcis saccharatus* of the pharmacopœia is prepared by digesting together one part of slaked lime, two parts of sugar, and twenty parts of water. The mixture is filtered, after standing for a few hours; and the filtered liquid contains one part of lime to sixty-five parts of the solution. It is administered in cases of chronic sickness and of sickness during pregnancy.

[1] Soubeiran, *Journ. Pharm.* [3], i. 649; Brendecke, *Arch. Pharm.* [2], xxix. 71.
[2] Berzelius, *Traité Chem.* v. 239.
[3] Peligot, *Compt. Rend.* xxxii. 335; Berthelot, *Ann. Chim. Phys.* [3], xlvi. 173.
[4] Dubranfaut, *Compt. Rend.* xxxii. 498.

The calcium sucrates, or saccharates of lime as they are commonly called, which play so important a part in the sugar manufacture, were first more closely examined by Peligot [1] and by Soubeiran.[2]

*Monocalcium Sucrate*, or *Monobasic Saccharate of Lime*, $C_{12}H_{22}O_{11}+CaO$, or $C_{12}H_{21}(CaOH)O_{11}$, is thrown down as an amorphous precipitate when alcohol is added to a solution containing equal molecules of sugar and lime. When dried in an atmosphere of carbon dioxide it forms a white, brittle, easily friable mass. To prepare the pure salt, a sugar solution containing an excess of lime is treated with magnesium chloride, when magnesium hydroxide is precipitated, and the monobasic saccharate remains in solution and is then precipitated by the addition of alcohol.[3] Monocalcium sucrate dissolves readily in cold water. On boiling the solution, the tribasic saccharate separates out, but dissolves again on cooling.

*Dicalcium Sucrate*, $C_{12}H_{22}O_{11}+2CaO$, or $C_{12}H_{20}(CaOH)_2O_{11}$, is obtained when a solution of sugar is treated with an excess of slaked lime and the filtrate precipitated by alcohol.[4] It separates from its hot concentrated aqueous solution on cooling in white crystals,[5] and dissolves at the ordinary temperature in thirty-three parts of water, but is more readily soluble in sugar solution, and the aqueous solution comports itself at the boiling point as does that of the monobasic compound.

*Tricalcium Sucrate*, $C_{12}H_{22}O_{11}+3CaO$, or $C_{12}H_{19}(CaOH)_3O_{11}$. The formation of this compound has already been described. It is obtained as a paste resembling coagulated albumen, and must be filtered hot and washed with hot water. When dried it forms hard brittle masses containing three molecules of water. If powdered caustic lime be added to a sugar solution containing alcohol, heat is evolved, and after standing sixteen hours the sugar and the lime have combined to form a granular mass of the tribasic sucrate.[6] It requires more than 100 parts of cold water for solution, and, on boiling, one-half of the salt separates out. It dissolves readily, however, in sugar-water. When boiled with alcohol it is converted into the anhydrous hexabasic saccharate.[7]

[1] *Ann. Chem. Pharm.* xxx. 71; *loc. cit.*; *Compt. Rend.* lix. 930.
[2] *Ann. Chem. Pharm.* xliii. 229.
[3] Benedict, *Ber. Deutsch. Chem. Ges.* vi. 413.
[4] Pelouze, *Jahresb.* 1864, 572.
[5] Boivin and Loiseau, *Ann Chim. Phys.* [4], vi. 203.
[6] *Neue Zeitsch. Rübenzucker*, iii. 178.
[7] Déon, *Bull. Chim.* xvii. 155.

*Strontium Sucrate*, $C_{12}H_{20}(SrOH)_2O_{11}$. When strontium hydroxide is added to a boiling 15 per cent. solution of sugar, the above compound begins to separate as soon as more than two molecules of strontia have entered into solution to each molecule of sugar present. When two and a half molecules of strontia have been added, almost the whole of the sugar is precipitated. Prepared in this way it forms a granular precipitate, which may be easily washed with hot water. If suspended in boiling water and allowed to cool, it decomposes slowly into its constituents. If, however, its solution be heated with strontia under pressure above 100° higher basic compounds are obtained (Scheibler).

*Barium Sucrate*, $C_{12}H_{21}(BaOH)O_{11}$. If a hot solution of one part of caustic baryta in three parts of water be mixed with the syrupy solution of sugar obtained by dissolving two parts of sugar in four parts of water the liquid solidifies to a crystalline mass. After washing with cold water and drying in an atmosphere free from carbon dioxide, the salt is obtained in glistening scales resembling those of boric acid. These have an alkaline taste, and, like the preceding compounds, are decomposed by carbon dioxide, sugar being again formed.[1]

The compounds of sugar with the alkalis and alkaline earths dissolve many bodies which are insoluble in water, especially metallic oxides, as, for instance, oxide of iron, oxide of copper, &c.,[2] whilst the salts of these metals in the presence of sugar are not precipitated by alkalis.[3] A solution of lime in sugar-water also dissolves carbonate, phosphate, and oxalate of lime.[4]

832 *Sucrates of Lead.* By digesting lead oxide with a sugar solution Berzelius obtained the compound $C_{12}H_{22}O_{11} + 2PbO$, or $C_{12}H_{20}(PbOH)_2O_{11}$, and when the lead oxide is present in excess all the sugar is precipitated.[5] This compound is also formed, according to Peligot, when sugar solution is precipitated with ammoniacal lead acetate, and the gelatinous precipitate thus obtained, dissolved in boiling water and the solution allowed to cool, the disaccharate separating out either in crystalline warty masses or in needles. It is insoluble in water, but dissolves readily in lead acetate solution. According to Peligot

[1] Peligot, *Ann. Chim. Phys.* [2], lxvii. 125 ; see also Stein, *Ann. Chem. Pharm.* xxx. 82.
[2] Hunton, *Journ. Prakt. Chem.* xi. 413 ; Boderbender, *Jahresb.* 1865, 600.
[3] Lassaigne, *Compt. Rend.* xiv. 691 ; Grothe, *Journ. Prakt. Chem.* xcii. 175.
[4] Bobbiere, *Ann. Chem. Pharm.* lxxx. 344.
[5] Dubranfaut, *Compt. Rend.* xxxii. 498.

this compound has the formula $C_{12}H_{18}Pb_2O_{11}$, but the above formula given to the compound by Berzelius has been verified by the researches of Mulder, who has also shown that this substance loses a molecule of water when heated to 165°.[1]

When caustic soda solution is added to a solution of sugar and lead acetate, the tribasic saccharate $C_{12}H_{16}Pb_3O_{11}$ is precipitated; this is somewhat soluble in boiling water and dissolves readily in caustic potash. It is also easily soluble in sugar-water, and from this solution the tribasic compound separates in needles (Boivin and Loiseau).

Lead is attacked by sugar solution, slowly at the ordinary temperature and more quickly at the boiling point, the lead passing into solution. Copper and zinc, on the other hand, are but slightly acted upon by sugar solution.[2]

*Sucrates of Iron.* Difficulty has often been experienced in carrying raw sugar in iron ships, as it has been found that the liquor leaking from the casks attacks, and rapidly corrodes, the iron plates. Moreover, it is a common observation in sugar refineries that the iron portions of machines are rapidly acted upon, or even completely dissolved, by the sugar solution. J. H. Gladstone,[3] who has investigated this subject, has found that when a piece of iron is partially immersed in a solution of sugar it is quickly attacked at the point of contact with the liquid, ferrous oxide passing into solution. This afterwards absorbs atmospheric oxygen and is precipitated as ferric oxide, whilst the sugar solution attacks a fresh portion of the iron. The sugar thus acts as a carrier of oxygen, and a small quantity of it is sufficient to corrode deeply a large plate of iron. The solution of ferrous sucrate is of a dark reddish-brown colour, and has the taste of the other ferrous salts. It is, however, not decomposed by alkalis, but sulphuretted hydrogen precipitates the iron completely as sulphide leaving pure sugar in solution.

In order to isolate the sucrate, Gladstone allowed iron to remain in contact with sugar solution in a warm place for eighteen months, when the whole became dry. This mass gave with water a tasteless solution, which possessed only a slight aftertaste of iron. It is not so readily altered in presence of oxygen as is the compound before described. The determi-

[1] *Journ. Prakt. Chem.* xix. 187
[2] Gladstone, *Quart. Journ. Chem. Soc.* vii. 195.
[3] *Quart. Journ. Chem. Soc* vii. 193.

nation of iron gave the formula $C_{12}H_{20}FeO_{11}$, but Gladstone is himself in doubt as to whether he was dealing with a pure compound. The same chemist found, further, that the presence of sodium chloride and other salts does not accelerate the corrosive action of sugar on iron, and that in fact the presence of these salts has no influence whatever on the reaction.

833 *Compounds of Sugar with Salts.* By evaporating a solution of sugar with common salt, Peligot in 1839 obtained deliquescent crystals, which, on analysis, he found to be a compound of equal molecules of the two bodies. Blondeau de Carolles then examined a similar body which, however, contained water of crystallization, of the presence of which Peligot made no mention. Neither Mitscherlich nor other chemists could, however, obtain either of these bodies, and the existence of this compound was held in question until Maumené [1] and Gill [2] succeeded in again obtaining it. For its preparation 85 parts of sugar and 15 parts of common salt are dissolved in water and the solution allowed to evaporate over sulphuric acid. It has the composition $C_{12}H_{22}O_{11} + NaCl + 2H_2O$, and crystallizes in rhombic prisms very readily soluble in water, but deliquescent only in very moist air. Gill in one preparation accidentally obtained crystals of the composition $2C_{12}H_{22}O_{11} + 3NaCl + 4H_2O$, but he could not obtain these again.

In addition to the above, the following compounds are known :

| | |
|---|---|
| $C_{12}H_{22}O_{11} + KCl + 2H_2O$ | rhombic non-deliquescent crystals.[3] |
| $2C_{12}H_{22}O_{11} + 3NaI + 3H_2O$ | large monoclinic crystals.[4] |
| $3C_{12}H_{22}O_{11} + Na_2B_5O_7 + 4H_2O$ | large crystals.[5] |
| $C_{12}H_{22}O_{11} + CuSO_4 + 2H_2O$ | small blue crystals.[6] |

## Ethereal Compounds of Saccharose.

834 Cane-sugar contains eight hydroxyls the hydrogen of which can be replaced by acid radicals.

*Tetranitroxysaccharose,* $C_{12}H_{18}(NO_3)_4O_7$. This compound, which is also termed nitro-sugar or fulminating cane-sugar,

[1] *Bull. Soc. Chim.* xv. 1.
[2] *Journ. Chem. Soc.* [2], ix. 269.
[3] Maumené, *Bull. Soc. Chim.* xix. 289.
[4] Gill, *loc. cit.*
[5] Stürenberg, *Ann. Chim. Pharm.* xviii. 279.
[6] Barreswil, *Journ. Pharm.* [3] vii. 29.

is obtained by acting on sugar with a mixture of concentrated nitric and sulphuric acids and is a resinous mass insoluble in cold water. At a low temperature it is brittle, but at the ordinary atmosphere temperature it forms an elastic mass which can be drawn out into fine threads exhibiting a fine silky lustre. It detonates when touched with a glowing body, and explodes on percussion. It is readily soluble in sulphuric acid, in strong nitric acid, in alcohol, &c. The formula above given for this body, although probable, has not as yet been definitely fixed.[1]

*Monaceto-saccharose,* $C_{12}H_{21}(C_2H_3O_2)O_{11}$, is formed when 2 parts of sugar, 1 part of acetic anhydride, and 6 to 8 parts of glacial acetic acid are heated together. On then adding ether, the acetate is precipitated as an amorphous mass, which is soluble in water and alcohol, and has a taste which is at the same time slightly sweet and bitter. When its ethereal solution is evaporated, an amorphous residue is obtained, consisting of a mixture of the tetracetate and the pentacetate.[2]

When sugar is heated with an excess of acetic anhydride, or with a mixture of sodium acetate and the anhydride, the hexacetate and the octacetate are formed.[3] These likewise are resinous bodies insoluble in water. They are saponified by potash solution with re-formation of cane-sugar.[4]

*Parasaccharose,* $C_{12}H_{22}O_{11}$. If a solution of sugar to which ammonium phosphate is added be allowed to stand exposed to the air a peculiar fermentation sets in and parasaccharose is formed, together with an amorphous deliquescent glucose. Parasaccharose is dextro-rotatory and forms small crystals which dissolve readily in water, but are insoluble in absolute alcohol.[5]

## MILK SUGAR, $C_{12}H_{22}O_{11}$.

835 Milk sugar, occurring in the milk of mammalia, especially in that of the herbivora, was first examined in 1619 by Fabrizio Bartoletti and termed by him *manna s. nitrum seri lactis.* It was more closely examined by Ludovico Testi, who in his *Relazione concernente il zuccaro di Latte,* published in 1698, recommends it as a valuable medicine.

[1] Schönbein, *Pogg. Ann.* lxx. 100; Sobrero, *Compt. Rend.* xxv. 122; Thompson, *Pharm. Journ. Trans.* viii. 165; Reinsch, *Jahrb. Prakt. Pharm.* xviii. 102; A. and W. Knop, *Journ. Prakt. Chem.* lvi. 334.

[2] Schutzenberger and Naudin, *Bull. Soc. Chim.* xii. 207.

[3] Herzfeld, *Ber. Deutsch. Chem. Ges.* xiii. 267.

[4] Demole, *ib.* xii. 1936.

[5] Jodin, *Comptes Rend.* liii. 1252.

According to Bouchardat, milk-sugar occurs, together with cane-sugar, in *Sapota achras*, a West Indian tree, also grown in other tropical countries for the sake of its fruit. Its milky sap in addition yields caoutchouc. Bouchardat examined a sugar-like substance, found amongst other specimens, with the label, "*Sucre obtenu de suc du sapotillier*, Martinique, 1837," and proved that it contained both sugars. From the ripe fruit, which he procured from Cairo, he obtained a sugar which, like milk-sugar, is transformed on oxidation into mucic acid, but which does not crystallize. Bouchardat therefore believed that the milk sugar is derived from the milky sap.[1]

Milk-sugar is prepared in large quantity, especially in Switzerland, from whey, this being simply evaporated to a syrup, and allowed to stand in a cold place. It is purified by re-crystallization, string or splinters of wood being placed in the solution, round which the crystals are deposited.

Commercial milk-sugar contains small quantities of other organic bodies and salts. In order to purify it is recrystallized and precipitated several times from aqueous solution by the addition of alcohol.

Pure milk-sugar forms large transparent rhombic crystals, which contain one molecule of water of crystallization. It has at 3·°9 a specific gravity of 1·534 and its co-efficient of cubic expansion from 0° to 100° is 0·00911 (Joule and Playfair). It dissolves in 6 parts of cold and 2·5 parts of hot water and has a much less sweet taste than cane-sugar. In alcohol it is insoluble.

If its aqueous solution be rapidly boiled it suddenly solidifies to a porous mass consisting of small crystals of the anhydrous compound.[2] This dissolves, with slight reduction of temperature, in as little as 3 parts of cold water, and from this solution crystals of the hydrated variety are quickly deposited.

When hydrated milk-sugar is heated to 130° it loses its water of crystallization and a white amorphous hygroscopic mass remains, which dissolves in water with an increase of temperature. If this solution be boiled, 4 parts of milk-sugar still remain in solution at 111°, but at 115° the liquid solidifies to a mass of the crystalline anhydrous sugar (Erdmann).

These isomeric modifications differ amongst themselves in their optical properties.

[1] *Bull. Soc. Chim.* [2], xvi. 36; Hofmeister, Hoppe-Seyler's *Zeitsch. Physiol. Chem.* i. 107( or 101).

[2] Schmögen, *Ber. Deutsch. Chem. Ges.* xiii. 1915; Erdmann, *ib.* 2180.

When milk-sugar is heated above 130° it acquires a yellow colour and at 180° it becomes brown, with formation of amorphous lactocaramel and separation of water.

Milk-sugar also becomes brown on heating with alkalis and it reduces alkaline copper solution. When heated with ammoniacal silver solution, the reduced metal forms a mirror-like deposit, and this reaction is used for silvering glass. When heated with water milk-sugar begins to decompose at 105°—110°, and at higher temperatures it yields the same products of decomposition as are found in the case of cane-sugar (Hoppe-Seyler).

When placed in contact with water and sodium amalgam it yields dulcite, mannite, isopropyl alcohol, and secondary hexyl alcohol. If boiled with dilute sulphuric acid it splits up into equal molecules of galactose and grape-sugar, water being eliminated. When heated with aqueous oxalic acid to 100° it is unaffected, thus differing from cane-sugar, and by this reaction the presence of the latter in a mixture of the two sugars can be detected.[1]

Milk-sugar does not undergo fermentation in the presence of pure yeast, but it is decomposed by certain schitzomycetes yielding alcohol and lactic acid,[2] the well-known intoxicating drink of the Tartars called koumiss being made from mare's milk.[3] A similar drink is now prepared in London, Switzerland, and other places from cow's milk, and much used as a dietetic for invalids. A sample of koumiss prepared in Davos was found on analysis to possess the following composition :—

| | |
|---|---|
| Water . . . . . | 90·346 |
| Alcohol . . . . . | 3·210 |
| Lactic acid . . . . . | 0·190 |
| Sugar . . . . . | 2·105 |
| Albuminates . . . . | 1·860 |
| Butter . . . . . | 1·780 |
| Salts . . . . . | 0·509 |
| Carbon dioxide . . . . | 0·177 |
| | 100·177 |

Old Russian koumiss contains more lactic acid and no sugar.[4]

[1] Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 75.
[2] Lorin, Fresenius's *Zeitsch.* xviii. 107.
[3] For its preparation, see *Pogg. Ann.* xxxii. 210.
[4] Suter-Naef, *Ber. Deutsch. Chem. Ges.* v. 286.

Milk-sugar is used for various purposes in medicine. Its aqueous solution mixed with cow's milk in certain proportions forms the essential feature of the artificial mother's milk now much in vogue. Human milk contains on an average 4 per cent. of milk-sugar.

836 *Metallic Compounds of Milk-Sugar.* Milk-sugar unites with the alkalis, the alkaline earths and lead oxide, forming compounds which, like those of cane-sugar, dissolve readily in water, but are insoluble in alcohol. Like cane-sugar it also prevents the precipitation of copper oxide, iron oxide, &c.

*Ethereal Compounds of Milk-Sugar.* Milk-sugar, like cane-sugar, contains eight hydrogen atoms which are capable of replacement by acid radicals.

*Nitroxylactose.* If milk-sugar be brought into a cold mixture of concentrated sulphuric and nitric acids and water be then added, a precipitate is formed which crystallizes in glistening scales from solution in alcohol.[1] According to Sokolow this is *pentanitroxylactose*, $C_{12}H_{17}(NO_3)_5O_{11}$; it melts at 140° and when the temperature is raised to 156° it explodes. At the same time amorphous *trinitroxylactose*, $C_{12}H_{19}(NO_3)_3O_{11}$, is formed; a body melting at 37° and at 110° decomposing with a powerful detonation.[2]

*Octacetolactose*, $C_{12}H_{14}(C_2H_3O_2)_8O_{11}$, is formed by heating milk-sugar with acetic anhydride and precipitating the solution with water, when *tetracetolactose* remains in solution and when dried forms a white, deliquescent granular powder.[3] The octo-compound is also obtained by heating milk-sugar together with the anhydride and anhydrous sodium acetate to 100°.[4] It crystallizes from a mixture of alcohol and ethyl acetate in rectangular tablets, and on saponification again yields milk-sugar. According to Demole, octacetolactose is also formed by the employment, instead of milk-sugar, of a mixture of grape-sugar and galactose obtained by the action of boiling dilute sulphuric acid on milk-sugar. Thus, it would appear that two glucoses may be re-united, with elimination of water, to form milk-sugar.[5]

[1] Reinsch, *Jahresb.* 1849, 470; Vohl, *Ann. Chem. Pharm.* lxx. 362.
[2] *Chem. Centralb.* 1882, 170.
[3] Schutzenberger and Naudin, *Bull. Soc. Chim.* xii. 208.
[4] Herzfeld, *Ber. Deutsch. Chem. Ges.* xiii. 266.
[5] *Ber. Deutsch. Chem. Ges.* xii. 1936.

## Melitose, $C_{12}H_{22}O_{11} + 3H_2O$.

337 This compound forms the Australian manna which exudes in drops from the *Eucalyptus mannifera* and other species of eucalyptus occurring in Tasmania where it is collected. It was first examined by Johnston in 1843, who assigned to the eucalyptus-sugar the formula $C_{12}H_{28}O_{14}$, and also showed that it contains water of crystallization,[1] whilst Berthelot, who studied it more closely in 1856, gave it the name it now bears.[2]

For the preparation of melitose, the manna is dissolved in hot water, the solution clarified by animal charcoal, and the filtered solution then allowed to crystallize. It forms fine felted needles, which give up two of their molecules of water at 100° and the remaining one at 130°, becoming, however, at this temperature yellow-coloured. Melitose has a slightly-sweet taste, dissolves in cold water in about the same proportion as mannite, and is readily soluble both in hot water and in alcohol. When boiled with dilute sulphuric acid, or when its aqueous solution is allowed to ferment in presence of yeast, it splits up into grape-sugar and eucalyn.[3]

## Melezitose, $C_{12}H_{22}O_{11} + H_2O$.

838 This sugar occurs in the manna of Briançon,[4] which in Southern France exudes in the summer from the young twigs of the larch (*Mélèze*, in French; *Abies Larix*) and is used as a substitute for sugar. Melezitose is also found in *turanibin*, a manna-like substance exuded from the *Alhazi Maurorum*, a shrub which grows in Persia and Affghanistan. This species of manna is brought into Lahore where it is used as a purgative. It contains, beside melezitose, cane-sugar and a syrupy matter.[5]

Melezitose is extracted from larch manna by boiling out with alcohol and is then recrystallized. It forms small, hard, glistening monoclinic crystals, which are about as sweet as grape-sugar and effloresce in the air. At 100° they lose their water of crystallization and they melt at 140°. When boiled with dilute sulphuric acid melezitose is converted into grape-sugar.

[1] *Mem. Chem. Soc.* i. 159.
[2] *Ann. Chim. Phys.* [3], xlvi. 66.
[3] *Ann. Chim. Phys.* [xvli.], 366.
[4] Berthelot, *Ann. Chim. Phys.* [3], lv. 282.
[5] Villiers, *Comptes Rend.* lxxxiv. 35.

## Mycose or Trehalose, $C_{12}H_{22}O_{11} + 2H_2O$.

839 In 1833 Wiggers found a sugar in ergot of rye (*Claviceps purpurea*), but its properties were then more closely studied by Mitscherlich, who gave to it the name mycose (μῦκος, fungus). Berthelot then examined *trehala manna*, which is obtained from the nest of a coleopterous insect (*Lavinus nidificans*), found in Syria upon a species of *Echinops*. The larvæ live on the sap, but exude the partly-digested food in order to make their nests. This nest is bag-shaped and about the size of an olive; the mass of which it is composed consists, together with a peculiar sugar, of a considerable amount of starch, some gum, and other substances.[1] In the East this trehala-manna is used as food and in Persia it is known as nest-sugar. Berthelot proved the distinct nature of this sugar and termed it trehalose,[2] and he afterwards recognised that it was identical with mycose.[3]

Trehalose also occurs in several species of fungus, as, for example, in the *Agaricus sulphureus*, which, when dried, contain 10 per cent. of this substance. In *Boletus cyanatus* mannite occurs together with mycose.[4]

To prepare trehalose, the trehala is boiled with alcohol, or the fungus is extracted with water; the solution is precipitated with lead acetate, the lead removed from the filtrate by means of sulphuretted hydrogen, and the solution then evaporated to a syrup.

Trehalose forms rhombic crystals, which melt when heated to 100°, and at 130° lose their water of crystallization and solidify. It dissolves easily in cold water, but is hardly soluble in cold alcohol. It possesses a sweet taste, and is transformed into grape-sugar when boiled with dilute sulphuric acid.

## Maltose, $C_{12}H_{22}O_{11} + H_2O$.

840 As early as 1811 Kirchhoff made the observation that starch may be converted into a crystalline sugar by treatment with dilute sulphuric acid.[5] Two years after this he found that the albuminous substance contained in grain is also able to effect this change, and, further, that the transformation is much more speedily effected when malted grain is used.[6] This starch-

[1] Gouibert, *Compt. Rend.* xlvi. 1213.
[2] *Ann. Chim. Phys.* [3], lv. 271.
[3] *Chim. Org.* ii. 263.
[4] Müntz, *Compt. Rend.* lxxvi. 649.
[5] *Schweigg. Journ.* iv. 108.
[6] *Ib.* xiv. 389.

sugar, which Saussure described more fully in 1819,[1] was at a later date considered to be identical with grape-sugar, until Dubrunfaut pointed out that the sugar from malt is more difficultly soluble in alcohol and exhibits a stronger rotatory power than grape-sugar, and that, therefore, it is a distinct substance, to which he gave the name of maltose.[2] The individuality of this substance was, however, first completely established by the researches of O'Sullivan.[3] Maltose is also, according to Dubrunfaut and others, the first product of the action of dilute sulphuric acid on starch (see Starch and Dextrin, pp. 554-563).

*Preparation.* For the preparation of maltose 2 kilograms of potato-starch are rubbed up with 9 liters of cold water and then heated in a water-bath until it forms a paste. When this has then cooled down to 60°—65°, from 120 to 140 grams of air-dried malt are added, and the mixture is kept at this temperature for an hour. It is next heated to the boiling-point, filtered hot, and the filtrate evaporated in shallow dishes until it attains the consistency of a syrup. This is then repeatedly boiled up with 90 per cent. alcohol. After a portion has been treated thus once or twice it is then extracted with absolute alcohol and the resulting solution is evaporated to a thin syrup which, after some days, crystallizes. The operation last described is, however, necessary only in cases where crystallized maltose is not to be had. In this case the alcohol is distilled off from the other extracts, the liquid evaporated to a syrup, and a small piece of crystallized maltose added. After the lapse of from three to five days the whole will have solidified to a thick paste, which is washed with methyl alcohol, thrown on to the filter pump, again washed with methyl alcohol, and then pressed. The residue, dried as completely as possible, is then dissolved on the water-bath, 30 cbc. of water being employed for every 100 grams of the material, 260 cbc. of 90 per cent. alcohol are next added, the liquid filtered hot, and the filtrate allowed to crystallize. The product is then further purified by recrystallization from hot alcohol or wood spirit.[4]

Maltose crystallizes in fine needles which become anhydrous at 100°, yielding an extremely hygroscopic residue. In aqueous solution it undergoes no change on treatment with malt extract,

[1] *Ann. Chim. Phys.* xi. 379. [2] *Ann. Chim. Phys.* xxi. 178.
[3] *Journ. Chem. Soc.* 1872, 579; 1876, i. 478; see also Schulze, *Ber. Deutsch. Chem. Ges.* vii. 1047. [4] Soxhlet, *Journ. Prakt. Chem.* [2], xxi. 274.

but when boiled with dilute sulphuric acid it is transformed into grape-sugar.[1] From the latter it is distinguished not only by its stronger rotatory power, but also by being less soluble in alcohol, and inasmuch as it does not reduce a weak acetic acid solution of copper acetate.

## THE GLUCOSES.

### Grape Sugar, or Dextrose, $C_6H_{12}O_6$.

841 So long ago as 1660, Glauber noticed that a granular sugar is contained in honey, in raisins, in inspissated must, and in the juice of sweet cherries. This substance was afterwards examined by various chemists, thus Löwitz pointed out that it differs from cane-sugar and that honey contains in addition a non-crystallizable sugar, whilst Proust in 1802 showed that the crystalline sugar of honey is identical with grape-sugar, and he classed cane-sugar, grape-sugar, and the non-crystallizable sugars, as distinct substances.

As has been already stated, Kirchhoff found in 1811, that starch may be transformed into a sugar, and Braconnot in the same year obtained it from linen rags.

More exact knowledge of these several varieties of sugar was obtained first, by the optical researches of Biot, and secondly by the more extended researches of Dubrunfaut.

The name *glucose* was suggested by Dumas, whilst Berthelot termed the left-handed or fruit sugar, *laevulose*, and Kekulé then designated the dextro-rotatory grape-sugar by the appropriate name of *dextrose*.[2]

As already described under cane-sugar, dextrose is very widely distributed throughout the vegetable kingdom, occurring almost invariably together with an equal quantity of laevulose forming invert-sugar, cane-sugar being also usually present (p. 497). The last-named sugar does not, however, occur in ripe grapes and cherries, these containing from 9·5 to 17 per cent. of invert-sugar. The amount of sugar and of acid contained in the various varieties of fruits has been determined by Fresenius[3] and by Buignet.[4]

Dextrose is also normally contained in small quantity in various animal fluids and tissues, occurring for example in the chyle, in the allantoic fluid, in urine, in the

[1] Compare Meissl, *Journ. Prakt. Chem.* [2], xxv. 123. [2] *Lehrb.* ii. 330.
[3] *Ann. Chem. Pharm.* ci. 219. [4] *Ann. Chim. Phys.* [3], lxi. 233.

liver, in eggs, &c. In cases of diabetes mellitus the urine contains as much as from 8 to 10 per cent. of grape-sugar, so that in the course of twenty-four hours the quantity of sugar eliminated often amounts to as much as 500 grams. Dextrose is also very frequently formed as a product of decomposition of the *glucosides*, a numerous class of bodies occurring chiefly in the vegetable kingdom. These by the action of dilute sulphuric acid or of certain ferments, are transformed, with assumption of water, into dextrose and other compounds. Some yield isomeric glucoses in place of dextrose. Dextrose is also a decomposition product of myronic acid.

For the preparation of small quantities of dextrose many recipes have been given. Of these the following yields a very pure product.[1] A mixture of 500 cbc. of 90 per cent. alcohol, and 20 cbc. of fuming hydrochloric acid is heated to 45°, and to this 160 grams of finely powdered cane-sugar are added in small quantities at a time, the heat being kept up till the whole is dissolved. After standing for about a week, crystals begin to appear; the mixture is then frequently agitated, and after about two days, a sufficient quantity of crystals having formed, the mother-liquor is removed by means of the filter pump. By means of these crystals the separation of the sugar in its preparation in larger quantity may be accelerated. For the preparation of a kilogram of the sugar, 12 liters of alcohol of 90 per cent. and 480 cbc. of fuming hydrochloric acid are heated on the water-bath to 45°, and 4 kilograms of powdered sugar added. When the whole is dissolved, the mixture is allowed to cool, and the crystals obtained in the previous preparation are then introduced, and the mixture frequently stirred round. A considerable quantity of very finely divided crystals separate out in the course of twelve hours, and after standing for twenty-four hours longer, the crystalline powder is separated from the mother-liquor by the filter pump, and washed with alcohol until all the hydrochloric acid is removed. Other methods of preparation have been described by Muller[2] and by Otto.[3]

842 *Manufacture of Starch Sugar.* Dextrose is prepared on the large scale by boiling starch with water containing from 1—2 per cent. of sulphuric acid, the operation being best conducted under pressure. The boiling is continued some little time after all the starch has disappeared, in order to allow of the conver-

[1] Soxhlet, *Journ. Prakt. Chem.*
[2] *Journ. Prakt. Chem.* [2], xxvi. 78. [3] *Ib.* 87.

sion into sugar of the dextrine which is first formed, this change however being in no case complete. The liquid is then neutralized with chalk or very finely-ground limestone, the filtrate decolorized, if necessary, with animal charcoal, and the solution evaporated, when the gypsum present in the liquid first separates out. This is allowed to settle, and the clear liquid is concentrated in a vacuum-pan until the point is reached at which it solidifies on cooling. As dextrose readily forms supersaturated solutions, its separation is accelerated by the addition of crystals of starch-sugar to the liquid. The material thus obtained contains in addition to water, dextrines and other products, the nature of which is not yet known. These are not fermentable, and they act upon the organism in a similar manner to fusel oil (Vol. III., Part I., pp. 148-288). The presence of the dextrines, which do not act injuriously, is due to the fact that these are the first products into which the starch is transformed, they being in turn transformed into dextrose. This latter change proceeds more quickly and completely according as the strength of the acid used is greater, the action longer, and the temperature to which the mixture is brought higher. When the final amount of starch decomposed to sugar varies from about 40 to 50 per cent. of the whole, the rate of change is proportional to the time allowed for the action. In the later stages of the operation the rate diminishes rapidly, so that the conversion of all the starch, even if under the circumstances it be possible, takes a long time. The cause of this slow action is to be ascribed to the amount of the resistance to change which the dextrines exhibit in contact with dilute acids.[1] Many attempts have been made to purify starch-sugar by re-crystallization and removal of the mother-liquor by pressure, as this cannot be effected by the centrifugal machine, because molasses are firmly inclosed between the plates of the sugar crystals.

Behr has recently made the important observation that when a few crystals of anhydrous grape-sugar, prepared by crystallization from alcoholic solution, are dropped into a solution of the sugar of sufficient concentration, heated to 30°—40°, the dextrose separates in anhydrous prisms. These are also formed when a solution of the moderately pure sugar is kept for some time at this temperature. The mother-liquor may be readily removed from these by drying in the centrifugal machine.[2]

[1] Allihn, *Journ. Prakt. Chem.* [2], xxii. 96.

[2] *Chem. News.* xlv. 179; *Ber. Deutsch. Chem. Ges.* xv. 1104; see also Hesse, *ib.* xv. 2349.

In order to prepare pure dextrose from commercial starch-sugar, the organic salts present must be decomposed by means of hydrochloric acid. The sugar is shaken with 85 per cent. alcohol to which 3 per cent. of hydrochloric acid has been added, when it becomes changed into a crystalline powder, whilst the liquid itself forms thin brown molasses. The liquid is removed by means of the filter pump, and the residue washed first with neutral alcohol of 85 per cent. and finally with such a alcohol of 90—95 per cent., this operation being naturally best performed on the filter pump. The brown molasses solution also deposits on standing pure dextrose in nodules.[1]

843 *Properties.* Dextrose crystallizes from aqueous solution with one molecule of water in thin six-sided scales which are aggregated in nodular- or cauliflower-like masses. From alcoholic solution anhydrous microscopic needles are obtained (Dubrunfaut) whilst from hot aqueous methyl alcohol, possessing at 20° a specific gravity of 0·825, triclinic prisms crystallize out, these usually being formed as twins.[2]

Dextrose dissolves at the ordinary temperature in about 1·2 parts of water, whilst in boiling water it is more readily soluble. One hundred parts of alcohol of specific gravity 0·837 dissolve 1·94 parts of dextrose at 17°·5, and 21·7 parts at the boiling-point. Grape-sugar has a taste that is less sweet than that of cane-sugar, the sweetness of this latter as compared with pure dextrose being according to Behr in the proportion of 1·66 : 1.

Anhydrous grape-sugar melts at 146° and passes at 170° into *glucosan*, $C_6H_{10}O_5$ or $C_{12}H_{20}O_{10}$, a colourless mass possessing hardly any sweet taste, and being again converted into dextrose when boiled with dilute acids.[3]

If a solution of dextrose in alcohol be cooled in ice, and then saturated in the dark with hydrochloric acid, *diglucose*, $C_{12}H_{22}O_{11}$, is produced, forming a very hygroscopic gum-like mass. When this is heated with water to 160°, it passes into a sugar, $C_6H_{12}O_6$, which differs from dextrose in that it possesses a very sweet taste, and it undergoes fermentation only with great difficulty.[4]

In aqueous solution dextrose is reduced to mannite by the action of sodium amalgam.[5] At the same time, ethyl alcohol, secondary propyl alcohol, hexyl alcohol, and lactic acid are also

[1] Schwarz, *Dingler's Polyt. Journ.* ccv. 427.
[2] Soxhlet and Brezina, *Journ. Prakt. Chem.* [2], xxi. 247.
[3] Gélis, *Compt. Rend.* li. 331.
[4] Gautier, *Bull. Soc. Chim.* [2], xxii. 145.
[5] Dewar, *Phil. Mag.* [4], xxxix. 345.

formed.[1] The substance last named is produced by the action of the caustic soda formed, for, if grape-sugar be heated on the water-bath with soda-ley, a violent reaction commences at 90° accompanied by increase of temperature, and lactic acid is formed, together with some formic acid, pyrocatechin, and other products.[2]

Dextrose, like cane-sugar, prevents the precipitation by alkalis of various metallic salts. From solutions containing gold and silver these metals are precipitated by dextrose on warming, whilst from an ammoniacal silver solution the metal is precipitated as a silver-mirror. Hence grape-sugar is used for silvering mirrors and other glass articles.

844 *Fehling's Reaction.* If to a solution of dextrose, first potash-ley and then copper sulphate be added, a deep blue solution is obtained which gradually in the cold, and instantaneously on heating, yields a precipitate of red cuprous oxide. This reaction is so delicate that 0·00001 gram of grape-sugar may be recognized by the formation of a precipitate and 0·000001 by the red coloration of the solution.[3] If to a solution of grape-sugar, there be added copper sulphate solution, soda-ley and an alkaline acetate, a precipitation of cuprous oxide also occurs on warming. Upon this reaction Barreswil[4] and Fehling[5] have grounded a method for the volumetric estimation of sugar, and this has been further worked upon and improved by various other chemists. It was formerly considered that one molecule of anhydrous dextrose had the power of reducing five molecules of cupric oxide to cuprous oxide, but according to Soxhlet this is not correct, as the quantity of cuprous oxide formed is dependent upon the concentration of the solution and upon other circumstances. In the application, therefore, of this reaction to the estimation of grape-sugar, care must be taken always to work as nearly as possible under the same conditions. For further details the subjoined memoirs may be consulted.

*Other Methods of Detection and Estimation.* When a solution of mercury cyanide, to which caustic soda solution has been

[1] Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 87.
[2] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* iv. 346.
[3] Trommer, *Ann. Chem. Pharm.* xxxix. 361.
[4] *Journ. Pharm.* vi. 361.
[5] *Ann. Chem. Pharm.* lxxii. 106; cvi. 75.
[6] *Journ Prakt. Chem.* [2], xxi. 254.
[7] Soxhlet, *loc. cit.* 289; Allihn, *ib.* [2], xxii. 52; Heron and Brown, *Chem. Soc. Trans.* 1879, 602.

added, is boiled with grape-sugar, metallic mercury is precipitated, and Knapp has applied this reaction to the volumetric estimation of dextrose,[1] whilst in place of the cyanide Sacchse has substituted a solution of potassium mercuric chloride.[2] Soxhlet, who has further worked out this method, has determined the conditions under which reliable results can be obtained by titration with alkaline mercury solution.[3]

If dextrose be boiled with caustic soda solution and basic bismuth nitrate then added, bismuth separates out as a black powder.[4] This reaction is useful in the detection of grape-sugar in urine, as the bismuth solution is not reduced either by uric acid or by creatinine, as is the case with copper solution. If, however, the urine contains albuminous bodies in which sulphur is present, black sulphide of bismuth will be formed, and these albuminous matters must therefore be removed before the test is applied. For this purpose freshly precipitated basic bismuth acetate is dissolved in hot potassium iodide solution with addition of a little hydrochloric acid. This liquid is then added to the urine, which has been previously acidified with hydrochloric acid, the precipitate which is formed filtered off, the filtrate supersaturated with caustic potash, and then heated to the boiling point.[5]

When a solution containing potassium ferricyanide and an excess of grape-sugar is heated, and baryta-water then added, the solution becomes colourless from formation of potassium ferrocyanide. If a solution of dextrose to which caustic soda has been added, be heated to 90°, and then a few drops of a solution of picric acid added, a red coloration is produced from formation of picramic acid. Laevulose and milk-sugar give the same reaction, but neither cane-sugar nor mannite.[7]

When an aqueous solution of dextrose is heated with chlorine or bromine and then with silver oxide, care being taken not to add an excess of the latter, a solution of *gluconic acid*, $C_6H_{12}O_7$ is formed, and this on evaporation remains behind as a syrup. It is a monobasic acid, but like the saccharoses it yields so-called basic salts.[8]

[1] *Ann. Chem. Pharm.* cliv. 252.
[2] *Farbstoffe, Kohlenhydrate*, &c., Leipzig, 1877, p. 214. [3] *Loc. cit.* 300.
[4] Böttger, *Journ. Prakt, Chem.* li. 431 ; see also Franqui and Vyverl, *Fresenius' Zeitsch.* v. 263. [5] Brücke, *Fresenius' Zeitsch.* xv. 101.
[6] Stahlschmidt, *Ber. Deutsch. Chem. Ges.* i. 141.
[7] Braun, *Fresenius' Zeitsch.* iv. 187.
[8] Hlasiwetz u Habermann, *Ann. Chem. Pharm.* clv. 121 ; clviii. 257 ; clxii. 301 ; Kiliani, *ib.* ccv. 182 ; Griesshammer, *Jahresb.* 1879, 852.

845 *Calcium Gluconate*, $(C_6H_{11}O_7)_2Ca + 2H_2O$, crystallizes in small needles united in warty masses. If slaked lime be added to its lukewarm solution, the liquid filtered and then heated to boiling, the salt $C_6H_{10}O_7Ca$ is almost completely precipitated.

On treatment with silver oxide and water gluconic acid is easily oxidized to glycolic acid, and by the action of commercial nitric acid it yields saccharic acid, oxalic acid, and *cassonic acid*, $C_5H_8O_7$. The last named acid, which may also be obtained from sugar, forms a syrup and is dibasic.[1]

*Paragluconic Acid* is produced when gluconic acid is left in contact for a long time with nitric acid of specific gravity 1·3. It likewise forms a syrup, but is distinguished from gluconic acid by the fact that it forms crystalline salts with the alkali metals, and non-crystalline salts with those of the alkaline earths, whilst with the first named acid the reverse is the case.[2]

*Uses of Starch-sugar.* Starch-sugar is made use of in the doctoring of wine. This treatment consists in diluting the sour must with water until the liquid contains only so much acid as is present in the juice of the good ripe grape, then adding the requisite quantity of sugar, and subjecting the liquor to fermentation. As ordinary starch-sugar always contains a large amount of unfermentable material which is strongly dextro-rotatory, doctored wine can easily be recognised by means of the polariscope.[3] A vinous drink is also obtained by another system, the grape skins being covered with a solution of starch-sugar solution and the liquid then allowed to ferment.

Starch-sugar is also used as a substitute for malt in the brewing of beer, in confectionery, for making table-syrups, artificial honey, &c. The solid sugar is also employed for the adulteration of powdered cane-sugar, and in the preparation of caramel. It likewise is used in calico-printing, for the reduction and fixation of indigo.

846 *Metallic Compounds of Dextrose.* If sodium ethylate be added to a solution of dextrose in absolute alcohol, a precipitate of $C_6H_{11}NaO_6$ is obtained, which on drying forms a friable exceedingly deliquescent powder.[4]

Lime and baryta dissolve readily in a solution of dextrose forming different compounds according to the quantity of the

[1] Siewert, *Jahresb.* 1859, 548; Hönig, *ib.* 666.
[2] Hönig, *Manatsh. Chem.* i. 49.
[3] Neubauer, *Fresenius' Zeitsch. Chem.* xv. 186.
[4] Hönig and Rosenfeld, *Ber. Deutsch. Chem. Ges.* x. 871.

base present, and these products are precipitated on the addition of alcohol. Dextrose also combines with copper oxide forming several compounds.[1]

Grape-sugar likewise unites with common salt, giving rise to a variety of compounds; $2C_6H_{12}O_6+NaCl+H_2O$ is frequently deposited from diabetic urine, and is easily obtained in large hexagonal crystals by allowing a concentrated solution, containing the constituents in the above proportion, to stand. Dextrose also combines with sodium bromide, but does not form compounds with the iodide.

*Ethereal Compounds of Dextrose.* Dextrose contains five alcoholic hydroxyls, whose hydrogen is capable of replacement by acid radicals.

*Dextrose Sulphuric Acid.* Dextrose dissolves in cold concentrated sulphuric acid without coloration, forming a dextrose sulphuric acid which yields soluble salts, and soon splits up, in aqueous solution, into the constituents from which it has been obtained.[2]

When dextrose is dissolved in chlorsulphonic acid, four-sided prisms are deposited after some little time, consisting of the chloride $C_6H_7Cl(SO_4H)_4O_6$. Milk-sugar, starch, dextrine, and cellulose also yield this compound when similarly treated. Cold water transforms this into the very unstable dextrose tetrasulphuric acid, $C_6H_7(OH)(SO_4H)_4O_6$, which forms amorphous salts. When the aqueous solution of this acid is warmed dextrose is again formed. If, however, the decomposition takes place at the ordinary temperature, dextrose trisulphuric acid $C_6H_7(OH)_2(SO_4H)_3O_6$, is formed as a first product. Its salts are amorphous and have a weaker power of rotation than those of the tetra-compound.[3]

*Acetates of Dextrose.* When dextrose is boiled with acetic anhydride, *diaceto-dextrose*, $C_6H_{10}(C_2H_3O)_2O_6$, and *triacetodextrose*, $C_6H_9(C_2H_3O)_3O_6$, are formed. These compounds, both of which are amorphous, may be separated by means of benzene, in which the last named is alone soluble.[4] If dextrose be heated with anhydrous sodium acetate and acetic anhydride to 100° *octaceto-diglucose*, $C_{12}H_{14}(C_2H_3O)_8O_{11}$, is formed, and this crystallizes from

[1] Salkowski, *Zeitsch. Physiol. Chem.* iii. 79; Fileti, *Ber. Deutsch. Chem. Ges.* viii. 441.
[2] Peligot, *Ann. Chem. Pharm.* xxx. 79.
[3] Claesson, *Journ. Prakt. Chem.* [2], xx. 18.
[4] Schützenberger and Naudin, *Bull. Soc. Chim.* xii. 204.

ether in cauliflower-like masses. It melts at 134° and on saponification yields diglucose (p. 540).[1]

By heating dextrose with glacial acetic acid to 100° for fifty hours, Berthelot obtained a liquid possessing an exceedingly bitter taste. This he supposed to be a hexacetyl compound, but it is, however, more probably *pentaceto-dextrose*, $C_6H_7(C_2H_3O)_5O_6$. Hydrochloric acid decomposes it into acetic acid and dextrose.

In a similar way Berthelot has prepared ethereal compounds of dextrose containing other fatty acids.[2]

*Acetochlorhydrose*, or *Acetochlordextrose*, $C_6H_7Cl(C_2H_3O)_4O_6$, is obtained by the action of acetyl chloride on anhydrous grape sugar. It forms a semi-fluid mass, which sometimes becomes crystalline, and is insoluble in water.[3] Cold concentrated nitric acid converts it into *aceto-nitrose* or *nitroxyacetodextrose*, $C_6H_7(NO_3)(C_2H_3O)_4O_5$, which crystallizes from a mixture of ether and alcohol in prisms or large tables.[4]

## Lævulose, or Fruit Sugar, $C_6H_{12}O_6$.

847 The history and modes of occurrence of this substance have already been given (p. 537).

For the preparation of lævulose the invert-sugar obtained when cane-sugar is heated with dilute sulphuric acid or hydrochloric acid is used. This inversion proceeds only in dilute solutions, and the heating must not be continued too long or by-products will be formed. According to Nicol, complete inversion is accomplished by dissolving 3 grams of sugar in 4 cbc. of water, adding 20 drops of hydrochloric acid of specific gravity 1·11, and heating the mixture on the water-bath for thirty minutes.[5]

To obtain the pure invert-sugar from the product obtained by the action of sulphuric acid, the acid must be removed by means of barium carbonate; or when hydrochloric acid has been used the solution is treated with silver oxide and the filtrate precipitated by sulphuretted hydrogen.

On evaporating these solutions, the invert-sugar is left behind as a colourless syrup. In the dark this remains unchanged, but on exposure to light dextrose separates out, and in

[1] Franchimont, *Ber. Deutsch. Chem. Ges.* xii. 1940; Hezfeld, xiii. 265.
[2] *Ann. Chim. Phys.* [3], lx. 89.
[3] Colley, *Compt. Rend.* lxx. 401.
[4] *Ib.* lxxvi. 437.
[5] *Fresenius' Zeitsch.* xiv. 177.

larger quantity the more intense the light is.[1] Honey, which consists principally of invert-sugar, exhibits a similar behaviour.

To prepare lævulose from the invert-sugar the following plan is recommended by Dubrunfaut. Ten grams of the sugar are dissolved in 100 cbc. of water, cooled down by ice-cold water, and agitated with 6 grams of finely-divided slaked lime. The difficultly soluble lime compound of lævulose which is thus formed separates out, whilst the corresponding dextrose compound remains in solution, and this latter may easily be removed by repeated pressing, &c. The lime compound is then decomposed by means of oxalic acid or carbon dioxide.[2]

Another method has been given by Girard, for the details of which the original paper may be consulted.[3]

Pure lævulose is also obtained from inulin, $C_6H_{10}O_5$, a substance which occurs in various plants (p. 566), or from its isomeride lævulan, which is found in the molasses of beetroot sugar, by treating these substances with dilute sulphuric acid.

Lævulose remains, on concentrating its solution, as a thick syrup which does not deposit crystals on keeping, and indeed it was believed that lævulose could not be obtained crystallized, until Jungfleisch and Lefranc succeeded in preparing it in this form. For this purpose the syrup is repeatedly treated with cold absolute alcohol, to remove water and certain admixtures. The residual syrup on being kept for some time in a cold place gradually deposits crystals and at last completely solidifies. This is then dissolved in hot alcohol when, on cooling, the greater part of the lævulose separates out as a syrup, but the mother-liquid yields, on further cooling, crystalline lævulose in thin needles, concentrically grouped and possessing a silky lustre. Lævulose may also be crystallized from aqueous solution, by bringing into the liquid a few of the crystals obtained as above described.[4] Crystalline lævulose melts at 95°, it is readily soluble in water and dilute alcohol, and possesses a taste as sweet as that of cane-sugar. By the action of sodium amalgam and water it is transformed into mannite, which is identical with the mannite found in nature, and also with that obtained from dextrose.[5] Like the last-named substance it reduces many metallic salts, but it differs from it in that lævulose is less easily fermentable on

[1] Scheibler, *Jahresb.* 1863, 574.
[2] *Bull. Soc. Chim.* xiii. 350.
[3] *Ib.* xxxiii. 154.
[4] *Compt. Rend.* xciii. 547.
[5] Krusemann, *Ber. Deutsch. Chem. Ges.* ix. 1465; Muntz and Aubin, *Ann. Chim. Phys.* [5], x. 559; Eug. Peligot, *Compt. Rend.* xc. 153.

addition of yeast, so that in a fermenting solution of invert-sugar the dextrose first disappears. Lævulose has the power of reducing copper oxide in the same proportion as dextrose, but the boiling must be kept up for thirty minutes (Allihn). It differs, however, from dextrose, inasmuch as that when treated in aqueous solution with chlorine or bromine it does not yield gluconic acid, but is oxidised to glycolic acid.

When lævulose is heated to 170°, it is converted into amorphous *lævulosan*, $C_6H_{10}O_5$. This substance is also obtained, together with dextrose, when cane-sugar is heated (p. 523), and if to a solution of the mixture yeast be added, the grape sugar alone enters into fermentation, and the lævulosan remains behind. On boiling with dilute acids lævulosan is again converted into lævulose.

848 *Metallic Compounds of Lævulose.* The most important of these is the calcium salt already mentioned, possessing the formula $C_6H_9(CaOH)_3O_6$. This forms acicular prisms which require more than 333 parts of cold water for solution. If from 12 to 15 grams of slaked lime be shaken up with a 6 to 8 per cent. solution of lævulose, at 20° filtered quickly, and the filtrate cooled down to 0°, crystals are obtained of $C_6H_{11}(CaOH)O_6 + 2H_2O$; these dissolve at 15° in 137 parts of water.[1]

By boiling a solution of invert-sugar with lime E. Peligot obtained a body which, according to him, is isomeric with cane-sugar, and to which he gave the name of *saccharin*.[2] Scheibler has however found that this substance, which may be obtained from either dextrose or from lævulose, but more easily from the latter, has the formula $C_6H_{10}O_5$, and is the anhydride or lactone of monobasic *saccharic acid*, $C_6H_{12}O_6$.[3] Saccharin is also formed when a solution of invert-sugar is allowed to stand in contact with lime for some months.[4] It also occurs in the molasses of beet-root sugar. It dissolves readily in water, possesses a saline bitter taste, and crystallizes in large rhombic prisms, which melt at 160—161°, and at a higher temperature sublime with partial decomposition. It is dextro-rotatory, and exhibits a neutral reaction, but its solution becomes acid on standing for some time, this change taking place more quickly if the liquid be heated. This change is due to the formation of saccharic acid, which however has not been obtained in the pure state, as it easily

[1] Eug. Peligot, *Compt. Rend.* xc. 153.
[2] *Compt. Rend.* lxxxix. 918.
[3] *Ber. Deutsch. Chem. Ges.* xiii. 2212.
[4] Kiliani, *ib.* xv. 2953.

splits up into water and saccharin. The salts of saccharic acid are lævo-rotatory, and many of them crystallize well.

If saccharin be heated with phosphorus and hydriodic acid, it is reduced to *saccharon*, $C_6H_{10}O_2$, an oily liquid boiling at 203°; this is probably the lactone of $\beta$-oxycaproic acid. Concentrated nitric acid oxidizes saccharin to the acid $C_6H_8O_6 + H_2O$, which forms large rhombic crystals, possessing a pleasant sour taste resembling that of citric acid. This acid is monobasic, but its solution when neutralized with alkali, becomes acid again on standing or more quickly on heating, and then requires a second equivalent of alkali for neutralization.

Saccharin has probably the following constitution :

$$\begin{array}{l} HO.CH_2.CH(OH).CH(OH).CH.CH_2.CO. \\ \qquad\qquad\qquad\qquad\qquad\quad \diagdown \quad \diagup \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O \end{array}$$

## GALACTOSE, $C_6H_{12}O_6$.

849 The fact that milk-sugar when boiled with dilute sulphuric acid does not yield grape-sugar, as was supposed to be the case, but a new sugar, was shown by E. O. Erdmann,[1] and by Pasteur,[2] and the latter chemist gave to this substance the name of *lactose*, which Berthelot changed to *galactose*, applying the term lactose to milk-sugar. According to him Bouchardat was the first to recognize the individuality of galactose.[3] Fudakowski then found that along with galactose another sugar is formed, and on further examination he recognized this to be dextrose.[4] Galactose is also formed by boiling certain kinds of gum-arabic with dilute sulphuric acid.[5]

In order to prepare galactose from milk-sugar, it is boiled with four times its quantity of water containing 5 per cent. of sulphuric acid for six hours, the solution neutralized with baryta, and concentrated by evaporation. This solution does not yield any crystals even after a week's standing, but if a few crystals of grape-sugar be introduced, the whole solidifies in a short time into a crystalline paste. This is remarkable, as the crystals formed are not those of dextrose but of galactose. The mass is then rubbed up with alcohol of 80 per cent., and the brown mother-liquor removed by filtration and pressing, these operations

[1] *Jahresb.* 1855, 673. [2] *Compt. Rend.* xlii. 347.
[3] *Chim. Org.* ii. 249.
[4] *Ber. Deutsch. Chem. Ges.* viii. 599 ; ix. 42 ; xi. 1069.
[5] Kiliani, *ib.* xiii. 2304 ; xv. 34 ; Claesson, *ib.* xiv. 1220.

being repeated until the residue is white; this is then dissolved in hot 70 per cent. alcohol and recrystallized.[1]

Galactose is readily soluble in hot, but much less soluble in cold, water, and crystallizes in large rhombic prisms. These possess a taste less sweet than that of cane-sugar, and melt at 142°—144°. In absolute alcohol and ether galactose is insoluble.

It is more strongly dextro-rotatory than dextrose, and like this it reduces alkaline solutions of copper, bismuth, and silver salts. By sodium amalgam it is transformed into dulcite,[2] whilst it is oxidized by nitric acid to mucic acid, and by bromine and water to monobasic *lactonic* acid, $C_6H_{10}O_6$. This last-named body, which is also obtained from milk-sugar, forms a crystalline deliquescent mass, and its soluble salts crystallize well.[3]

*Calcium Lactonate*, $(C_6H_9O_6)_2Ca + 7H_2O$, forms monoclinic tables.[4] Its lukewarm solution dissolves lime, and on then heating the salt $C_6H_8O_6Ca$ separates out.

## Arabinose, $C_6H_{12}O_6$.

850 By boiling gum-arabic with dilute sulphuric acid, Biot and Persoz[5] obtained a sugar, which Berthelot thought was galactose.[6] Scheibler, however, further examined this gum-sugar, and stated it to be a new substance and termed it arabinose.[7] Kiliani, on the other hand, considered that the sugar obtained from gum was indeed galactose.[8] Clæsson explained these contradictory statements by finding that whilst galactose is certainly formed from such varieties of gum as yield mucic acid on oxidation, yet other varieties of gum arabic do yield arabinose.[9]

Arabinose crystallizes from hot alcohol in radiating prismatic tufts, it melts at 160°, is more strongly dextro-rotatory than galactose, and is oxidized by nitric acid to oxalic acid, without first yielding mucic acid.

The gum of the cherry-tree when boiled with dilute sulphuric acid first yields *cerasinose*, $C_6H_{12}O_6$, which separates

[1] Soxhlet, *Journ. Prakt. Chem.* [2], xxi. 262.
[2] Bouchardat, *Ann. Chim. Phys.* [4], xxvii. 79.
[3] Barth and Hlasiwetz, *Ann. Chem. Pharm.* cxxii. 96.
[4] Kiliani, *Ber. Deutsch. Chem. Ges.* xiv. 651.
[5] Bouchardat, *Ann. Chim. Phys.* [2] lii. 85.
[6] *Loc. cit.*
[7] *Ber. Deutsch. Chem. Ges.* vi. 614.
[8] *Loc. cit.*
[9] *Loc. cit.;* Kiliani, *Ber. Deutsch. Chem. Ges.* xv. 34.

from solution in hot alcohol in very brittle and hygroscopic crystals, and these even at 100° become brown and soften. It passes on long standing into arabinose, the same change occurring when cerasinose is heated for two hours to 100° with water acidified by hydrochloric acid.[1]

### Eucalyn, $C_6H_{12}O_6 + H_2O$.

851 This is formed together with dextrose by boiling melitose with dilute sulphuric acid, and as it does not enter into fermentation by contact with yeast, it may be readily separated from the dextrose formed at the same time. Eucalyn is a thick syrup which has only a slightly sweet taste. It is turned brown by alkalis and reduces alkaline copper solution.

### Sorbin, $C_6H_{12}O_6$.

852 Pelouze found this substance in the juice from mountain-ash berries which had been collected in September, the liquid having been allowed to stand by itself for a year.[2] The fresh juice of the ripe berries does not contain sorbin,[3] which is probably formed in the course of fermentation as a reduction product of sorbite, $C_6H_{14}O_6$, (p. 492).

Sorbin forms hard rhombic crystals, and possesses as sweet a taste as cane-sugar. It is soluble in half its weight of water, but is only slightly soluble in alcohol. It is coloured brown on heating with alkalis, and reduces an alkaline copper solution. Its solution does not ferment on the addition of yeast. If the solution be treated with chlorine and then with silver oxide glycollic acid is obtained.[4] By concentrated nitric acid it is oxidized to dextro-rotatory tartaric acid, racemic acid, oxalic acid, and *aposorbic acid*, $C_5H_8O_7$; this last named acid is dibasic, and cystallizes in rhombic scales melting at 110°.

### Inosite, $C_6H_{12}O_6 + 2H_2O$.

853 This substance was first found by Scheerer in the fluid contained in the muscles of the heart of the ox

[1] Martin, *Sacchsé's Phytochem. Unters.* 78.
[2] *Ann. Chem. Pharm.* lxxxiii. 47.
[3] Byschl, *Jahresb.* 1854, 664.
[4] Hlasiwetz and Habermann, *Ann. Chem. Pharm.* clv. 129.
[5] Dessaignes, *Ann. Chem. Pharm.* Suppl. ii. 242.

(ἴς, gen. *ἰνός*, muscle),[1] and according to Sokolow and Panum, it does not occur in any other muscular fluid.[2] It is however, found widely distributed in the animal kingdom, as for instance in the lungs, the liver, the spleen, and the kidneys of the ox,[3] in the brain of the same,[4] in the urine of man in case of Bright's disease (Cloëtta), and even in healthy urine after drinking large quantities of water.[5]

Inosite is also frequently found in the vegetable kingdom. Vohl discovered it first in the young French bean (*Phaseolus vulgaris*), and gave to the new saccharine substance the name of *Phaseomannite*, and soon afterwards he recognized its identity with inosite.[6] Marmé then found it in the unripe pea, the lentil, and the fruit of the Robinia (*Robinia pseudacacia*), in the white cabbage, foxglove, dandelion, in asparagus, and in the germ buds of the potato.[7] It also occurs in the grape, and hence, as it is not fermented by yeast, it finds its way into wine.[8] It is likewise present in vinous liquids,[9] as well as in the young leaves of the vine,[10] and in the leaves of the ash,[11] and of the walnut tree.[12]

To prepare inosite from the heart or the lungs of the ox, the material is finely chopped up, and exhausted with water, some acetic acid added, and the mixture then heated to the boiling point. The filtrate is treated with neutral lead acetate, filtered off from the precipitate formed, and then the filtrate is precipitated by basic lead acetate, the washed precipitate decomposed by sulphuretted hydrogen, and the concentrated solution precipitated by addition of alcohol. It is prepared from vegetable juices by neutralizing the liquid with baryta-water, treating with lead acetate solution, and then proceeding as above described. To precipitate the substance from the concentrated aqueous solution, Hilger recommends a mixture of 10 parts of alcohol and 1 part of ether.

Inosite forms large transparent monoclinic crystals, which possess a sweet taste, and are soluble at the ordinary temperature in about 6 parts of water. Inosite is but slightly soluble in

[1] Dessaignes, *Ann. Chem. Pharm.* lxxiii. 322.
[2] *Ib.* lxxxi. 375.
[3] Cloetta, *Ann. Chem. Pharm.* xcix. 289.
[4] Müller, *ib.* ciii. 140.
[5] Kültz, *Fresenius' Zeitsch.* xvi. 135.
[6] *Ann. Chem. Pharm.* xcix. 125; ci. 50; cv. 330.
[7] *Ib.* cxxix. 222.
[8] Hilger, *ib.* clx. 333.
[9] Canstein and Neubauer, *Ber. Deutsch. Chem. Ges.* vi. 1411.
[10] Neubauer, *Fresenius' Zeitsch.* xii. 45.
[11] Gintl, *Jahresb.* 1868, 800.
[12] Tanset and Villiers, *Bull. Soc. Chim.* xxix. 74.

hot dilute alcohol, and it is insoluble in absolute alcohol and in ether. It effloresces in the air and becomes completely dehydrated at 100°. When boiled with alkalis it is not coloured brown, and it has no action on an alkaline copper solution. Nitric acid oxidizes inosite to oxalic acid. Its solution yields with lead acetate a gelatinous precipitate which, after drying over sulphuric acid, possesses the empirical formula $2\,C_6H_{12}O_6 + 5\,PbO$ (Cloëtta).

If inosite be evaporated almost to dryness with addition of a little nitric acid, a few drops of ammoniacal calcium chloride solution then added, and the mixture again evaporated, a rose-red coloration is produced, and in this way the presence of 0·0005 grams of inosite may be recognized. This reaction is not yielded by other saccharine bodies or by starch.[1] If to a few drops of inosite one drop of a mercury nitrate solution (used in the estimation of urea) be added, a yellow precipitate is formed which on heating becomes red; this becomes yellow again when cold, but reddens when re-heated.[2]

*Hexnitroxyinosite*, $C_6H_6(NO_3)_6$. Inosite is dissolved by concentrated nitric acid, and on addition of sulphuric acid to this solution a gritty precipitate is formed which is insoluble in water. If this be dissolved in hot alcohol, the hexnitrate crystallizes out on cooling in rhombic tables and prisms, and these explode violently on percussion. The mother-liquor yields on evaporation fine white needles of the *trinitrate*, $C_6H_9O_3(NO_3)_3$.[3] The formation of this hexnitrate proves that inosite is the alcohol of a hexad radical.

## Scyllite, $C_6H_{12}O_6$.

854 This compound occurs in largest quantity in the kidney of the skate, shark (*Raja batis* and *clavata*), and dogfish (*Scyllium canicula*), and also of the *Spinax acanthias*, and it also occurs in the liver, milt, &c., of these cartilaginous fishes. It may be prepared from these sources by the method described for the extraction of inosite. It is less soluble in water than the last-named substance, and crystallizes in anhydrous monoclinic prisms which have a slightly sweet taste. Like inosite it

[1] Scherer, *Ann. Chem. Pharm.* lxxxi. 375.
[2] Gallois, *Fresenius' Zeitsch.* iv. 264.
[3] Vohl, *loc. cit.*; *Ber. Deutsch. Chem. Ges.* vii. 106.

is neither coloured brown by alkalis, nor does it reduce alkaline copper solution, but it does not yield Scherer's reaction for inosite.[1]

## Dambose, $C_6H_{12}O_6$.

855 This glucose occurs as the monomethyl ether in caoutchouc from Borneo and as the dimethyl ether in that from the Gaboon, the native name for which is *n'dambo*. The dambose is obtained from the ethers by heating them with fuming hydriodic acid. It is easily soluble in water, but insoluble in absolute alcohol. It crystallizes in six-sided prisms, which possess a sweet taste, and on heating melt at 212° without decomposition. It is not affected by boiling alkalis. With concentrated nitric acid it yields an explosive nitrate, but by the hot acid it is oxidized to saccharic acid.

*Dambose Methyl Ether*, or *Bornesite*, $C_6H_{11}(CH_3)O_6$. By subjecting Borneo caoutchouc to pressure, a liquid is obtained from which bornesite is left on evaporation. It dissolves easily in water, is slightly soluble in alcohol, and crystallizes in rhombic prisms which have a sweet taste, and melt at 175°.[2]

*Dambose Dimethyl Ether*, or *Dambosite*, $C_6H_{10}(CH_3)_2O_6$, is similarly contained in aqueous solution in raw Gaboon caoutchouc, and is obtained on evaporation of the liquid. It is very sweet in taste; and crystallizes from hot spirit in anhydrous hexagonal prisms, and from water in oblique prisms which contain three molecules of water. The anhydrous compound melts at 195° and by careful heating may be sublimed between 200° and 210° in long needles.[3]

*Metezodambose*, $C_9H_{18}O_9$, occurs as the methyl salt, termed matezite, $C_9H_{17}(CH_3)O_9$, in Madagascar caoutchouc. This body melts at 235°, is feebly dextro-rotatory, and closely resembles dambose.[4]

[1] Städeler and Frerichs, *Journ. Prakt. Chem.* lxxiii. 48.
[2] Girard, *Compt. Rend.* lxxiii. 426.
[3] *Ib.* lxvii. 820.
[4] Girard, *Bull. Soc. Chim.* xxi. 219.

# THE AMYLOSES.

## STARCH OR AMYLUM, $(C_6H_{10}O_5)_n$.

856 Starch was known to the Greeks. They denoted this substance by the word ἄμυλον (*a*, privative, and μύλος, a millstone), as it is prepared as a fine flour without grinding. Dioscorides relates that the best kind of starch-flour is obtained from Cretan or Egyptian wheat, the grain being steeped in water until the husk is softened, after which it is kneaded and washed with water. The husk is then removed by sieving, and the powdery deposit at once placed on bricks and dried in the sun, as when moist it soon turns sour. Similar statements are made by Pliny, who adds that starch was discovered in Chios. Beccari in 1745 proved that wheaten flour yields gluten as well as starch when washed.

Starch is widely disseminated throughout the vegetable world. It is formed from the protoplasm contained in the chlorophyll cells, and is therefore found in all phanerogams, whilst it scarcely occurs in any of the cryptogams which do not contain chlorophyll. These organs, which serve as reserve material from which the young shoots of the plant obtain nourishment, are rich in starch, and hence it collects during autumn in the medullary rays of the wood, in tubers and roots and in many fruit and seeds.

The solid particles of starch being the first recognizable products of assimilation are noticed beneath the surface of the green chlorophyll corpuscles.[1] Each solid particle grows into a starch granule, which only increases in size as long as it is in contact with the protoplasm, and on exposure to light at suitable temperatures, ranging from 15° to 25°. This formation of starch may be followed through the various organs and tissues of the plant. If leaves of certain delicate plants be covered for

[1] Sachs' *Flora*, 1862; *Experimental Pflanzen-physiolgie*, 1865; also Naegeli, *Zeitschr. f. Wissen. Bot.* iii. and iv.

some days, it will be seen that the starch granules have disappeared ; if, then, the leaf be exposed to direct sunlight the starch granule makes its appearance in certain cases in about five minutes,[1] whilst in diffused light this takes about two hours. This appearance of the starch granule takes place more quickly under the influence of the yellow rays than under those of the blue.[2] According to Schimper[3] it appears that in the deeper lying parts of plants where no green chlorophyll exists, the starch grains are found in connection with minute granules of protoplasm termed by him starch-formers; these differ from chlorophyll corpuscles mainly in not possessing a green colour, and in having a much more delicate structure. The starch-grain grows in part at the expense of the chlorophyll corpuscles and of the starch-formers, in both cases the protoplasm becoming altered and diminished in quantity. It seems probable, however, that a series of products intervene between the commencement of assimilation, the decomposition of carbonic acid, and formation of starch, although the existence of such intermediate substances has not yet been proved.

857 *Manufacture.* Starch is usually manufactured in Europe from wheat, maize, rice, and potatoes, and, in tropical countries, from the stems of the palm and from tubers of various plants.

The oldest method of manufacturing starch is that of the acid fermentation. This process is in use at the present day in countries in which a meal-tax exists. The grain is first softened by steeping, and when sufficiently soft it is crushed between rollers, and then coarsely ground and moistened with water, after which it is placed in a large vat, when fermentation sets in. Acetic, lactic, and butyric acids are thus formed from the sugar, and from a part of the starch, of the grain, whilst the gluten loses its tenacity so as to admit of the separation of the starch by washing. The mass is then washed in a revolving cylinder having holes in the sides, and the milky liquid allowed to settle in a vat, in which the starch, having settled down, is again washed by decantation.

Another process consists in first softening the grain by soaking and then crushing it between rollers and washing out the starch, which, as it contains gluten, is allowed to stand until this substance has been decomposed by fermentation.

[1] Kraus, *Jahrbuch f. Wissen. Bot.* vol. vii.
[2] Sachs' *Text-Book of Botany*, Macmillan & Co.
[3] *Bot. Zeitung*, 1880, p. 881.

A third plan is to use flour which must first be kneaded to a dough; this, after washing on sieves and between rollers, is brought into a centrifugal machine, where the washing is completed. In order to purify the starch thus obtained it is treated with water containing some caustic soda, and then passed through a sieve which retains the gluten and other impurities (O. Jones).

*Maize-starch* is chiefly manufactured in England (Brown and Polson), and in the United States (Erkenbrecher and the Glen Cove Co.), the operations being identical with those described. *Rice-starch* is also prepared in a similar way, the separation of the gluten being facilitated by washing with dilute caustic soda. For the preparation of *potato-starch*, the tubers are ground to pulp and then washed on sieves or on a centrifugal washer. The wash-water is made sour by sulphuric acid, and the starch afterwards heated with water containing $\frac{1}{350}$ of its weight of caustic soda. Starch can also be obtained from horse-chestnuts in a similar way. In the East Indies, the Philippine Islands, &c., starch is prepared from the pith of the sago-palm (*Sagus lævis*, or *Sagus rhumphii*). This comes into the market under the name of *sago* (a word meaning *bread*). *Arrowroot* is the starch of the *Maranta arundinacea* and *indica*, and a few other tropical plants growing in the West Indies, Brazil, and the Southern States. *Tapioca* is derived from the *Jatropha manihot*, this, like sago, being subjected to pressure to give the grains a peculiar form.

858 *Properties.* Starch is a white glistening powder which, except in the case of potato starch, which contains traces of a volatile oil, is devoid of taste and smell.

The size of starch granules varies considerably. The largest granules occur in potato starch and in one kind of sago from *cauna gigantea*, and these have a diameter varying from 0·14 to 0·185 mm. The granules of wheaten starch, on the other hand, are usually from 0·014 to 0·05 mm. in diameter, but the largest granules of wheaten starch are always larger than the smallest granules of potato starch. The smallest granules are those of beet-root and rice, which have a diameter of from 0·002 to 0·015 mm. But whilst the size of the granule varies in every species of starch, each species exhibits its own peculiar form, which can readily be detected under the microscope. Not only is this the case, but adulteration and its amount can thus be ascertained. Thus the adulteration of the more expensive wheaten starch with cheaper potato starch is capable of precise measurement.

Starch granules have the power of polarizing light like a doubly refracting crystal. The granule consists of a series of layers arranged round a nucleus; this stratified structure cannot

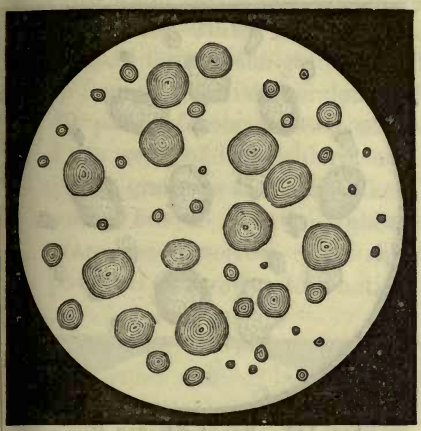


FIG. 138.—Wheaten starch, 300 diams.

FIG. 139.—Potato starch, 300 diams.

always be observed in the granules, but is rendered perceptible by treatment with dilute alkali, or with chromic acid.

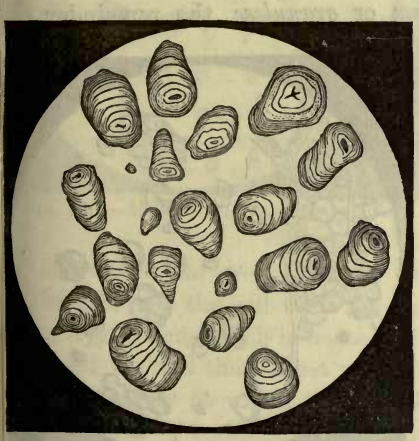


FIG. 140.—St. Vincent arrowroot, 300 diams.

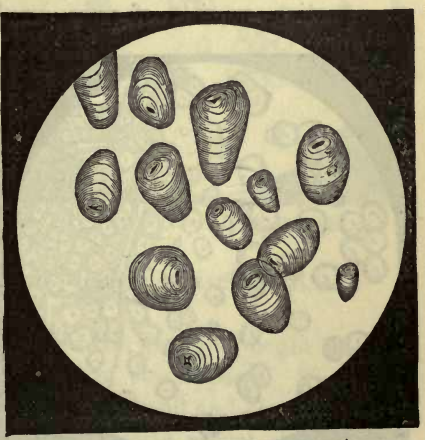


FIG. 141.—St. Thomas arrowroot, 300 diams.

So long ago as 1716 Leeuvenhoek asserted that the cell-wallo of the granules differ from the cell-contents, and Raspail confirmed this assertion, believing however that the cell-contents were identical with gum-arabic.[1] On the other hand, Guibort

[1] *Nouv. System. Org. Chim.* 1833.

came to the conclusion that both the above possessed the same chemical composition, and that they only differ physically.[1] The structure of the starch granule was then carefully examined

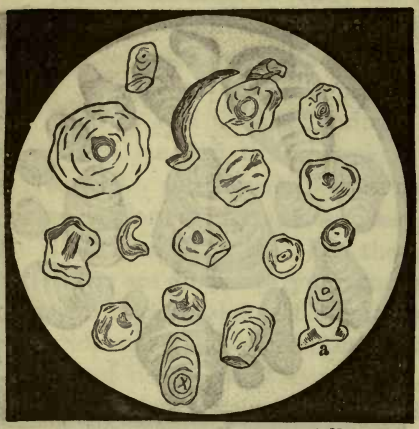



FIG. 142.—Sago starch (partially gelatinized), 300 diams.

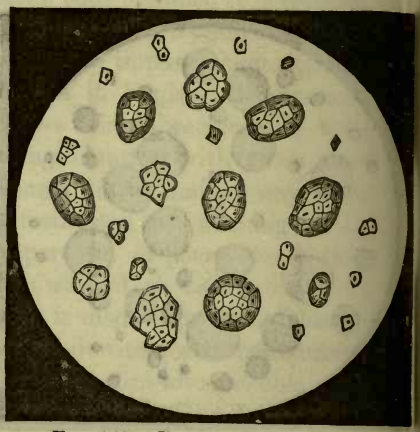


FIG. 143.—Rye starch, 300 diams.

by Fritsche,[2] and the classical researches of Naegeli[3] proved that starch is a mixture of several isomeric compounds. The chief portion consists of pure *amylum* or *granulose*, the remainder

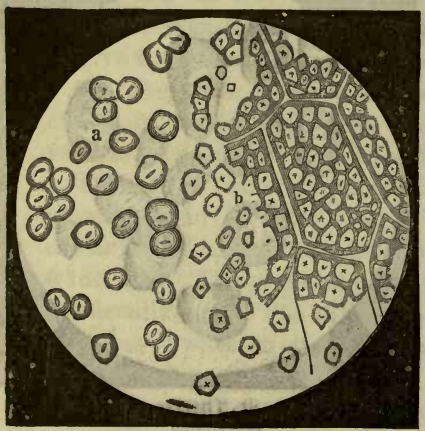



FIG. 144.—Maize starch, 300 diams.
(a) From the outer portion of the grain.
(b) From the inner mealy portion.

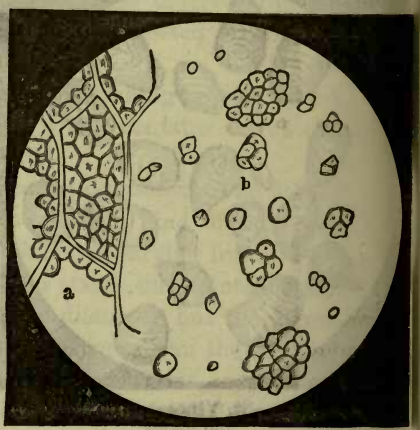



FIG. 145.—Rice starch, 300 diams.
(a) A portion of the cellular tissue.
(b) Free starch grains.

being made up of *starch cellulose* or *farinose*. These bodies do not, however, differ essentially from each other but, as will be

[1] *Journ. Chim. Med.* v. 9. [2] *Pogg. Ann.* xxxii. 129. [3] *Jahresber.* 1859, 544.

shown, are connected together by a variety of intermediate products.[1]

When starch is brought in contact with acidified water or with water containing certain ferments, the granulose dissolves completely, whilst the starch cellulose remains behind in the original form of the granule. This separation requires from two to four days for its completion if 1 part of starch be mixed with 40 parts of concentrated solution of common salt, containing 1 per cent. of hydrochloric acid and the whole heated to 60°.[2] If the granules are not broken, starch is not acted on by cold water, but if they be rubbed up with water a part of the granulose dissolves. This solution can be filtered and has a powerful dextro-rotatory action. The longer the treatment is

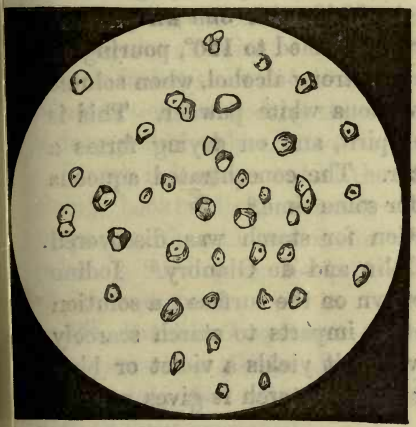


FIG. 146.—Millet starch, 300 diams.

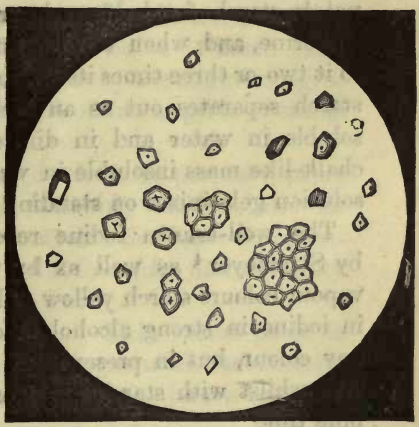


FIG. 147.—Buckwheat starch, 300 diams.

continued, the greater is the portion which dissolves until, at length, only the cell-walls remain.

859 When starch is heated with water the granules begin to swell up, and then burst with formation of starch-paste. The temperature at which the granules begin to swell and also that at which a complete transformation into paste occurs, differs according to the nature of the starch. As a rule, the swelling begins at about 50° and is completed at from 60° to 70°. In the case of barley starch, however, the change begins at 37°·5 and is finished at 62°·5, whereas the starch from acorns does not

[1] Naegeli, *Beiträge zur näheren Kenntniss der Stärke Gruppe.* Leipzig: Engelmann, 1864.

[2] Schulse, *Sachsse's Farbstoffe, Kohlenhydrate, &c.* p. 123.

appear to swell until 57°·5, and is not completely resolved into paste below 87°·5.[1]

To produce an even starch-paste the starch is first rubbed up intimately with a small quantity of water to form a creamy mass and then boiling water added. If this paste be treated in the cold with extract of malt, the granulose dissolves and the farinose remains. Soluble starch is also formed when starch-paste is boiled with water, and the same change takes place to a certain extent when the paste is allowed to stand for a long time. The insoluble portion is soluble in caustic potash, and when this alkaline solution is boiled it is resolved into soluble starch,[2] a change which is also accomplished by the action upon starch, of acids, zinc chloride, &c.

Soluble starch is best obtained by heating sixty grams of potato-starch for half an hour to 190° with one kilogram of glycerine, and, when the mixture has cooled to 120°, pouring on to it two or three times its volume of strong alcohol, when soluble starch separates out as an amorphous white powder. This is soluble in water and in dilute spirit, and on drying forms a chalk-like mass insoluble in water. The concentrated aqueous solution gelatinizes on standing for some time.[3]

The well-known iodine reaction for starch was discovered by Stromeyer[4] as well as by Colin and de Glaubry.[5] Iodine vapour colours starch yellow or brown on the surface; a solution in iodine in strong alcohol or ether imparts to starch scarcely any colour, but in presence of water it yields a violet or blue tint, whilst with starch-paste or soluble starch it gives a deep blue tint.

According to Naegeli that portion of the granulose which is coloured blue by iodine is first brought into solution by dilute acids. This portion, which has the greatest attraction for iodine, is contained in largest quantity in potato-starch, and this always becomes coloured first. When a change is effected by acids, the insoluble portion assumes a violet tint. On further action of acid the residue is coloured red by iodine, and after a time this changes to a reddish yellow tint, the residue then consisting of starch cellulose.

The several kinds of starch consist of varying mixtures of these different modifications. Potato-starch contains more of

[1] Lippmann, *Journ. Prakt. Chem.* lxxxiii. 51.
[2] Brown and Heron, *Chem. Soc. Trans.* 1879, p. 596.
[3] Zulkowsky, *Ber. Deutsch. Chem. Ges.* xiii. 1395.
[4] *Schweigg Journ.* xii. 349. [5] *Ib.* xiii. 453.

the "yellow" than of the "blue" modification and only small quantities of the intermediate varieties. Wheaten starch gives a violet coloration with iodine, as the amount of the "blue" substance present is only small, whilst a larger proportion of the "red" and "violet" modification is contained, but on boiling with water the "blue" substance is formed.[1]

The blue colour of starch-paste or of soluble starch disappears when the liquid is warmed and returns when it is cooled, so that the reaction is most delicate when the liquid is coldest. A solution containing 0.00000002 grm. of iodine is turned perceptibly blue at 0°, but not at 13°. At the latter temperature the colour is first observed with 0·000003 of iodine, and at 30° 0·000009 is needed. Iodide of starch is not a chemical compound, its formation depending on surface-attraction, like that exhibited by wood-charcoal for colouring matters. The decolorization on heating is explained by the fact that iodine is much more soluble in hot than in cold water, and also by the slighter degree of attraction exerted by the starch. Bromine imparts to starch a deep yellow colour.

Starch is largely used in the arts, for laundry purposes, paper sizing, bookbinding, weaving and finishing calicoes, also for preparing the thickening for colours and mordants in calico-printing, for dusting the forms in metal founding, and a variety of other purposes.

860 *Metallic Compounds of Amylum.* Thin starch-paste is precipitated by alkalis, alkaline earths, ammoniacal solution of lead acetate, &c. The compounds thus obtained have been but very slightly examined.

*Ethereal Salts of Amylum.* When cold sulphuric acid acts upon starch flour several acid sulphates are formed; these yield amorphous salts.[2]

*Nitrates of Amylum.* Braconnot, by the action of concentrated nitric acid on starch flour, prepared a body which he believed was obtained from starch without any diminution in weight. To this he gave the name of Xyloidine (ξύλον wood; εἶδος like)[3] because it appeared to resemble woody fibre. Liebig, however, showed that this body contains the elements of nitric acid[4] and Pelouze[5] found that 100 parts of starch yield from 128 to 130 parts of xyloidine. Analysis shows that this body consists of a

[1] *Liebig's Ann.* clxxiii. 218.
[2] Blondeau de Carolles, *Ann. Chem. Pharm.* lii. 416; Fehling, *ib.* lv. 13.
[3] *Ib.* vii. 245. [4] *Ib.* vii. 249. [5] *Comptes Rendus*, vii. 713; xxiii. 890.

mixture of the mononitrate $C_{12}H_{19}(NO_3)O_9$ and the dinitrate $C_{12}H_{18}(NO_3)_2O_8$. Béchamp then proved that the latter compound exists in an insoluble and a soluble modification.[1] The first is prepared by rubbing 1 part of dry starch with 5 to 8 parts of fuming nitric acid, and mixing the semi-fluid mass with from 20 to 30 parts of water. The curdy mass is then washed with water and dissolved in a mixture of 10 parts of glacial acetic acid and 1 part of an acetic acid of 69 per cent. On the addition of water a white powder is precipitated only soluble in the above-mentioned mixture of acid. To prepare the soluble dinitr-oxyamylum 10 to 12 parts of fuming nitric acid must be used, the pasty mass is then precipitated by water, washed, dried and dissolved in ether-alcohol. This modification also dissolves in glacial acetic acid, and in various other solvents, but not in strong spirit. Both bodies explode when heated to about 200°.

Béchamp has also prepared a tetranitrate $C_{12}H_{16}(NO_3)_4O_6$ in both a soluble and an insoluble modification. They also explode when heated to 273° and decompose slowly at ordinary temperatures. All these nitrates are reconverted into starch by the action of ferrous chloride solution in presence of some iron filings.

*Hexaccto-Amylum*, $C_{12}H_{14}(C_2H_3O_2)_6O_4$. This compound is formed when starch-flour is heated to 150° with acetic anhydride. It is a white powder insoluble in water and not coloured by iodine, but saponified by alkalis with formation of insoluble starch which gives the iodine reaction. If the temperature to which the above mixture be heated rises to 160° a higher acetate is not formed, but the isomeride *Hexacetodextrine*.[2]

## Paramylum $(C_6H_{10}O_5)_n$.

861 This body occurs in the infusoria *Euglena viridis* which forms a green scum on the surface of the water in which it grows. It exists in the form of colourless granules, which dissolve in caustic potash and are reprecipitated unchanged on acidifying the solution. They are not coloured by iodine, remain unaltered in presence of diastase or of dilute acids, but when boiled with concentrated hydrochloric acid they yield a fermentable sugar.[3]

[1] *Ann. Chim. Phys.* [3], lxiv. 311.
[2] Naudin and Schützenberger. *Compt. Rend.* xlviii. 814.
[3] Gottlieb, *Ann. Chem. Pharm.* lxxv. 51.

## THE DEXTRINES, $(C_6H_{10}O_5)$.

862 In 1811 Vauquelin pointed out that starch can be converted by heating into a substance resembling gum arabic; about the same time Kirchhoff found that when starch is boiled with dilute sulphuric acid a crystallizable sugar is formed, and soon after Vogel showed that in this latter reaction a gum-like body is also produced. That the gluten contained in wheaten and other grain has the power of effecting a similar change on starch, and that this is brought about more quickly by malted grain, was also noticed by Kirchhoff in 1814. Payen and Persoz were the first to isolate the active principle of malt, and to this, in 1833, they gave the name of *diastase*, as they believed the action of this body to be a simple separation (*διάστασις*) of starch from the granule.[1] Shortly before this, Biot and Persoz had examined starch gum, and had given to it the name of *dextrine*, from its dextro-rotatory power.[2] They supposed that this body, an isomeride of starch, is the first product of the change of this latter body to sugar, so that by the action of dilute acids dextrine is converted into sugar by the assumption of the elements of water, and this view was generally adopted. But in 1860 Musculus proved it to be incorrect, as he showed that dextrine and sugar are formed simultaneously. This fact was doubted until O'Sullivan[3] proved the truth of the view enunciated by Musculus, and also showed that the sugar which is first produced from starch is not dextrose, as had been believed, but maltose. According to this observer, the following equation represents the action when an infusion of malt has acted on starch paste for from five to ten minutes at 63°:

$$C_{18}H_{30}O_{15} + H_2O = C_{12}H_{22}O_{11} + C_6H_{10}O_5.$$

At temperatures between 64° and 70° the following change occurs provided the mixture be quickly cooled after complete fluidity occurs:

$$2C_{18}H_{30}O_{15} + H_2O = C_{12}H_{22}O_{11} + 4C_6H_{10}O_5.$$

[1] *Ann. Chim. Phys.* [2], liii. 73. [2] *Ib.* [3], lii. 72.
[3] *Journ. Chem. Soc.* 1876, ii. 125.

About 95° the diastase ceases to be active. At temperatures near to this the decomposition occurs as follows :

$$4C_{18}H_{30}O_{15} + H_2O = C_{12}H_{22}O_{11} + 10C_6H_{10}O_5.$$

The dextrine thus formed passes, on longer contact with the malt infusion, into maltose.

Märker appears to have come to different conclusions concerning the nature of these changes. He found that more maltose and less dextrine were produced at lower temperatures than at higher ones.[1]

Further experiments of Musculus and Gruber led to the supposition that the starch is first converted into a soluble modification containing five or six times the molecule $C_{12}H_{20}O_{10}$, and that this is converted, by assumption of water, into one molecule of maltose, and into *erythrodextrine*, a body coloured red by iodine. This is again converted, by assumption of water and elimination of maltose, into *achrodextrine*, a body not coloured by iodine; and this in its turn is converted, by a similar set of changes, into other achrodextrines, until at last all is converted into maltose. Each of the dextrines thus obtained is distinguished from the preceding by its specific rotation being less marked, whilst its cupric reducing-power in alkaline solution becomes stronger.[2]

Similar observations have been made by Brown and Heron, who have fully examined this question. According to them it appears probable that the simplest formula for soluble starch is $10(C_{12}H_{20}O_{10})$. From this molecule one molecule of maltose and of *α-erythrodextrine* are first formed; this latter being then split up, by absorption of water, into maltose and *β-erythrodextrine*. In this way the destruction of the original starch proceeds with formation of seven achrodextrines until, finally, only maltose is present.[3] On the other hand, O'Sullivan [4] assumes that in the action of diastase upon starch we have not to do with a destruction of a complex molecule, but that both starch and dextrine have the molecular formula $C_{12}H_{20}O_{10}$, and that the molecules in solution are arranged in a series of molecular aggregates, some of which are split up by the action of diastase, whilst others again unite themselves to form *α*-dextrine. According to the same chemist, soluble starch is prepared by

[1] *Landw. Versuchstat*, xxii. 69. [2] *Bull. Soc. Chim.* xxx. 54.

[3] Contributions to the history of starch and its transformations, *Chem. Soc. Journ.* 1879, i. 596.

[4] On the transformation products of starch, *Chem. Soc. Journ.* 1879, i. 770.

heating starch paste at 73-74° C. with the least possible quantity of the cold-water extract of malt until the solution has become clear, then heating to boiling, and filtering. The solution is then evaporated until a skin forms, and on cooling a brilliant white powder separates out, which may be purified by washing with cold water, frequent solution in hot water, filtration, &c.

*Amylodextrine* is a similar body obtained by Naegeli by boiling "yellow" starch with water. On cooling, or preferably on freezing, particles having a diameter of 0·035 mm. separate out. These polarize light like starch, and consist of small needles, which may also be obtained by adding alcohol to the aqueous solution. When dried over sulphuric acid they possess the composition $C_{36}H_{62}O_{31} + H_2O$, and they lose the molecule of water at 100°. They are coloured yellow by iodine, but their solution becomes first violet and then red in contact with this reagent, showing that two modifications exist, which can be separated by partially precipitating the coloured solution by means of sodium acetate.[1]

From the foregoing it appears that in spite of the numerous investigations on this subject we are still in doubt as to the exact nature of the various intermediate products which make their appearance in the change from starch to maltose.

Commercial dextrine usually consists mainly of erythrodextrine, but contains other constituents besides this as well as starch and sugar. It is generally prepared from potato-starch, though other cheap starches are used. It is prepared in various ways.

*Calcined farina* or *British gum*, a substance largely used in various manufacturing processes as a cheap substitute for gum arabic, is obtained by heating starch to a temperature of from 210° to 280°; the product prepared at a low temperature is less coloured than that exposed to a greater heat, but the process is a slower one. If the starch flour be moistened with dilute acid, the change to dextrine takes place at from 100° to 125°. Most of the dextrine in the market is now made by this process, a mixture of nitric and hydrochloric acids being generally used, though either of these or oxalic acid may be employed. Infusion of malt may likewise be used for the same purpose, but this practice is not so common.

Dextrine is either a white or yellowish-white powder, or a translucent, brittle mass, easily soluble in water, yielding a clear mucilage, which is precipitated by alcohol. This aqueous solution

[1] *Liebig's Ann.* clxxiii. 218.

is converted into maltose in presence of diastase, this change being also effected on boiling with dilute acids; but by further action this changes into dextrose. This latter can be reconverted into an achrodextrine by dissolving the dextrose in concentrated sulphuric acid and precipitation with a 95 per cent. alcohol, the dextrine separating out as a white amorphous mass readily soluble in water. This dextrine possesses twice the rotatory power of dextrose, into which it again is transformed by boiling with dilute sulphuric acid.[1]

When dextrine, and therefore also starch and bread, is roasted, a soft, amber-coloured, soluble body, termed by Reichenbach[2] *assamar*, is formed. According to Gélis a brown, brittle mass of *pyrodextrine*, $C_{48}H_{74}O_{37}$, is formed under similar circumstances.[3]

*Sinistrine*, $(C_6H_{10}O_5)_n$, is a body resembling dextrine, found in the squill (*Urginea scilla*). It is lævo-rotatory, is not coloured by iodine, and yields lævulose when boiled with dilute sulphuric acid.[4]

*Lichinine* $(C_6H_{10}O_5)_n$. This body, also known as moss-starch, occurs in Iceland-moss (*Cetraria islandica*). It is soluble in hot water, but separates on cooling in a gelatinous form.[5] The lichen also contains another substance, *isolichinine*, soluble in cold water, but insoluble in alcohol; it is distinguished from the foregoing compound by being tinted blue by iodine.[6]

## Inulin $(C_6H_{10}O_5)_n$.

863 In 1804 Valentine Rose[7] obtained a white powder from the roots of elecampane (*Inula helenium*), "which stands between starch and sugar in its properties." To this Thomas Thomson gave the name of inulin, whilst its composition was ascertained by Mulder. This body appears to replace starch in the roots of many species of *Compositæ*, occurring in the dahlia tubers (of which as much as 10 per cent. by weight consists of inulin); in those of the Jerusalem artichoke (*Helianthus tuberosus*); in the roots of the dandelion (*Taraxacum officinale*); in chicory (*Chicorium intybus*). Inulin is also found in the fleshy stems of different species of the *Cacalia* and *Kleinia*, in the woody

[1] Musculus, *Bull. Soc. Chim.* xviii. 68.
[2] *Ann. Chem. Pharm.* xlix. 1.
[3] *Ann. Chim. Phys.* [3], lii. 388.
[4] Schmiedberg, *Hoppe-Seyler's Zeitschr.* iii. 112.
[5] Knop and Schnedermann, *Ann. Chem. Pharm.* lv. 165.
[6] Berg, *Jahresb.* 1873, 848.
[7] Gehlen, *Journ. Chem.* iii. 217.

stalks of *Musschia*, in the herbaceous stalks of *Stylidium suffruticosum* and *Selliera radicans*.[1]

For the preparation of inulin the tubers of dahlia are boiled out with water, to which some lime is added, and the concentrated extract frozen. After thawing, the brown deposit is dissolved in hot water, the liquid again frozen, and the operation repeated three or four times. The concentrated mother-liquors yield more inulin. The powder is washed first with dilute spirit, then with alcohol of 93 per cent., and lastly with ether-alcohol, after which it is dried in vacuum over sulphuric acid.[2]

Inulin is a snow-white powder consisting of sphæro-crystals, soluble in hot water, but only slightly so in cold, and insoluble in absolute alcohol. It is very hygroscopic, and when dried possesses the composition $(C_6H_{10}O_5)_6 + H_2O$, or $C_{36}H_{62}O_{31}$. It is not coloured blue by iodine; its solution possesses lævo-rotatory power, and on boiling with dilute acid it is transformed into lævulose; diastase, however, does not effect this change.

## Lævulin, $C_6H_{10}O_5$.

864 This compound, which occurs together with inulin in the tuber-bearing *Synantherea*, as dahlia and Jerusalem artichoke, was first prepared by Ville and Joulie.[3] It was then examined by Popp, who classed it as a saccharose, and termed it synanthrose.[4] Diek and Tollens afterwards determined its exact composition.[5]

To prepare this substance the expressed juice of the ripe tubers is precipitated with lead acetate, the filtrate heated with sulphuretted hydrogen, and the solution evaporated after neutralization with magnesia. Lævulin is extracted from the residue by boiling dilute alcohol, whilst the inulin remains insoluble. Lævulin is also found in the young rye grain; it diminishes in quantity as the corn becomes ripe, whilst the starch increases in amount.[6]

Lævulin is an amorphous deliquescent body, possessing an insipid taste, and is converted on boiling with dilute acids into dextrose and lævulose. Its solution is optically inactive, and it enters slowly into fermentation in presence of yeast, being first decomposed into the two glucoses.

[1] *Ann. Chem. Pharm.* xxviii. 278.
[2] Kiliani, *Liebig's Ann.* ccv. 145.
[3] *Bull. Soc. Chim.* [2], vii. 262.
[4] *Ann. Chem. Pharm.* clvi. 181.
[5] *Ibid.* cxcviii. 228.
[6] Müntz, *Compt. Rend.* lxxxvii. 679.



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*Triticin* $(C_{12}H_{22}O_{11})_n$, is also an amorphous substance, possessing lævo rotatory power and yielding lævulose on boiling with acid. It is found together with invert-sugar in couch grass (*Triticum repens*).[1]

## Glycogen, $(C_6H_{10}O_5)_n$.

865 This substance, sometimes called animal starch, was discovered by Claude Bernard in human liver as well as in that of graminivorous animals. He gave to it the name of *matière glycogène*, because, after the liver is freed from sugar by washing, a substance is found which yields sugar with a ferment also present in the liver.[2] Since then glycogen has been shown to exist very widely diffused throughout the animal kingdom, indeed it appears to be an essential accompaniment of cellular growth,[3] occurring in large quantity in the fœtus.[4] It also occurs in blood and muscular tissue.[5] Moreover it is found in mollusca; thus, dried oysters are said to contain as much as 9·5 per cent. of glycogen.[6] This substance has also been detected in the vegetable kingdom, in moulds and other fungi.[7]

To prepare glycogen the fresh liver of an animal, slaughtered soon after a meal, when it is richest in glycogen, is finely cut up and boiled out with water, and the extract treated first with a solution of potassium mercury iodide and afterwards with hydrochloric acid, and this repeated until no further precipitate occurs, in order to separate out the nitrogenous materials. The glycogen is then precipitated by adding alcohol to the filtrate, the powder being washed with alcohol first of 60 per cent., then of 95 per cent., and lastly with ether.[8] As boiling water dissolves glycogen only slowly, it is preferable to use caustic potash solution, and then to treat the solution, having been neutralized with hydrochloric acid, as above.[9] The nitrogenous constituents can be separated by boiling with zinc chloride, when the glycogen remains unaltered.[10]

Glycogen is a white amorphous powder possessing, when dried

[1] H. Muller, *Jahresb.* 1873, 832.
[2] *Jahresb.* 1857, 552.
[3] Hoppe-Seyler, *Physiol. Chem.* 1877, i. 82.
[4] McDonnell, *Proc. Roy. Soc.* xii. 476; xiii. 371.
[5] Nasse, *Zeits. Physiol. Chem.* iii. 201.
[6] Bizio, *Zeitschr. Chem.* 1866, 222.
[7] *Nature*, November 1, 1883.
[8] Brucke, *Jahresb.* 1871, 843.
[9] Wittich, *Zeitsch. Anal. Chem.* xiv. 227.
[10] Abeles, *Zeitsch. Anal. Chem.* xvii. 500.

over calcium chloride, the composition $C_{12}H_{20}O_{10} + H_2O$,[1] but losing its water at 100°.[2] It dissolves in water, forming an opalescent liquid, which becomes colourless on addition of acetic acid; this solution is powerfully dextro-rotatory, and is coloured wine-red by iodine. On boiling with dilute hydrochloric[3] or sulphuric acid, glycogen is converted into dextrose,[4] whilst, by contact with diastase, dextrine, maltose, and dextrose are formed, these bodies occurring in the liver examined after the rigor-mortis has occurred.[5] The dextrine which Limpricht found in horse-flesh[6] was in all probability a product of decomposition of glycogen.[7]

## THE GUMS, $(C_6H_{10}O_5)_n$.

866 The substances classed under the above head occur widely distributed throughout the vegetable world, but seldom in animal bodies. They are amorphous, insoluble in alcohol, but either dissolve in water or swell up when placed in this menstruum. They are not coloured by iodine, and when boiled with dilute sulphuric acid they are converted into glucoses.

*Arabin*, or *arabic acid*, is the chief constituent of gum arabic, which exudes from the bark of several species of acacia growing in tropical countries. The finest specimens of this gum come from Egypt and Senegal, less pure varieties from Morocco and the Cape. Gum arabic is also imported from Australia, but the largest amount comes from Egypt and the Red Sea ports on the Arabian coast, whence its name.

The ancient Egyptians were acquainted with this gum and termed it Kami, using it in painting. Theophrastus mentions that *κόμμι* is a product of a tree called *ακανθα*, and Celsus in the first century terms it *gummi acanthium*. The word gum arabic is used for the first time by Diodorus Siculus in speaking of the products which had to pay duty at the Roman custom-house in Alexandria. It was certainly shipped in early times from the Gulf of Aden to Arabia, where it was used as a medicine.

[1] Bizio, *loc. cit.*
[2] Kekulé, *Jahresb.* 1858, 570.
[3] Berthelot and Luca, *Jahresb.* 1859, 627.
[4] Maydl. *Zeitsch. Physiol. Chem.* iii. 196.
[5] Musculus and Mering, *ibid.* ii. 403.
[6] *Ann. Chem. Pharm.* cxxxiii. 294.
[7] Demant, *Zeitsch. Physiol. Chem.* iii. 200.

The best Cordovan or Egyptian gum comes into the market in the form of round or egg-shaped lumps about the size of a walnut. These are colourless or slightly yellow and cracked throughout the mass, easily breaking in irregular masses, having a glassy fracture. The Senegal gum is found in larger masses, which are less friable than gum arabic.

Gum arabic leaves on burning a residue of about 3 to 4 per cent. of ash consisting of the carbonates of potassium, calcium, and magnesium ; these metals being contained in the gum as salts of arabic acid. This consists at least of two varieties, as solutions of the different kinds of gum deviate the ray of polarized light some to the right and some to the left.

Arabic acid may be prepared from mucilage by adding hydrochloric acid and precipitating with alcohol, dissolving this in water containing the same acid, and repeating this several times. It may also be obtained by dialysing the acid solution. In the moist state arabic acid is a milk-white mass, having an acid reaction and setting free carbon dioxide from carbonates. It is soluble in water, but after drying it swells up in contact with water, dissolving again on addition of lime-water or baryta-water. An aqueous solution of pure arabic acid is not thrown down on addition of alcohol alone, but the presence of a few drops of hydrochloric or nitric acid or of a salt solution occasions an immediate precipitate.[1] Arabin dried at 100° has the composition $C_{12}H_{22}O_{11}$, and at 120° it loses one molecule of water.[2]

Silkworms and other insects contain gum of a similar character.[3]

Gum arabic is used for the same purposes as dextrine, also in medicine to prepare pastes and syrups, and for a variety of purposes in the arts, for giving lustre to crape, for colours, and in the preparation of ink, as holding the insoluble tannate of iron in suspension. This last property of gum may be easily shown by adding sulphide of ammonium to a mixture of gum mucilage and a solution of sugar of lead ; the black opaque liquid does not deposit a precipitate on standing, and is not decolourized on filtration.

867 *Metarabic Acid*, or *Cerasin*, is the substance, insoluble in pure water but soluble in alkaline liquids, obtained by heating gum arabic to 100°. Cerasin occurs, together with arabin, as a

[1] Neubauer, *Ann. Chem. Pharm.* cii. 105. [2] Gélis, *Compt. Rend.* xliv. 144.
[3] *Ann. Chem. Pharm.* cxi. 26.

lime compound in the insoluble part in cherry-tree gum, and also in sugar-beet and other fleshy roots. To prepare it from beetroot the press-cake is broken, repeatedly extracted with alcohol, the solution being each time expressed, and boiled with water to drive off the alcohol. On the addition of milk of lime, and on warming on the water-bath, the metarabic acid is converted into arabin; the filtrate is then freed from lime by carbonic acid, the clear liquid evaporated with acetic acid, and the arabin precipitated by alcohol. It is difficult thus to obtain the arabin free from inorganic constituents; to effect this a partial precipitation by alcohol must be made, and the precipitate allowed to stand with the solution, and in a few weeks the whole of the mineral matter is found in the precipitate.[1] The arabic acid thus prepared is more powerfully laevo-rotatory than any other kind of gum arabic, and is probably a pure compound.

*Dextran*, or *fermentable gum*, is found in unripe beetroot,[2] and it is also formed in the mucic fermentation of sugar, and in the lactic fermentation.[3] Dextran likewise not unfrequently separates out as a jelly-like body in the working of the beetroot-sugar process, and is often found in considerable quantities in molasses, from which it can be separated by addition of water and hydrochloric acid, and precipitation with alcohol (Scheibler). It is an amorphous substance, readily soluble in water, powerfully dextro-rotatory, and slowly yielding dextrose when boiled with acid.

868 *Parabin*, $C_{12}H_{22}O_{11}$, is found in carrots and beetroot, and in larger quantities in *agar-agar*, or Ceylon moss, in a seaweed (*Gracilaria lichenoides*) used in China and India for making soups, jellies, &c., and now seen in European markets.[4] The name *gelose*[5] was given to this body by Morin and Porumbaru. Parabin is also found in an edible alga from Swan River (*Gigartina speciosa*). It was formerly thought that this and other algæ yielded the material of the celebrated Chinese birds' nests, but it is now ascertained that the swallows themselves secrete the material of which the nests are made.

To prepare parabin the beet press-cake is washed with water and spirit, then extracted with a 1 per cent. hydrochloric acid, and precipitated by alcohol. It is a powder which swells up to

[1] Scheibler, *Ber. Deutsch. Chem. Ges.* vi. 612.
[2] *Ib. Wagner Jahresb.* 1875, 790.
[3] Brüning, *Ann. Chem. Pharm.* civ. 197.
[4] Reichardt, *Ber. Deutsch. Chem. Ges.* viii. 807.
[5] *Compt. Rend.* xc. 924, 1081.

a jelly in contact with water, dissolves in dilute mineral acids, and is precipitated by alkalis or alcohol. It is further distinguished from arabin by the facts that it does not exhibit an acid reaction, does not decompose carbonates, and does not yield arabinose when boiled with dilute sulphuric acid, whilst on long continued warming with alkalis it passes into arabin.

869 *Wood gum.* This substance is found as mucilage largely diffused throughout the vegetable kingdom. After drying, this gum is insoluble in cold water and ammonia, but dissolves slowly in 50 parts of boiling water, and readily in caustic soda. Its alkaline solution exhibits lævo-rotatory power. When boiled with dilute sulphuric acid, it yields a glucose possessing copper-reducing power, but incapable of entering into fermentation with yeast.[1]

According to Singer all varieties of woods and woody tissues also contain a gum which is soluble in water and resembles arabin.[2]

*Bassorin* occurs in Bassora gum, which is derived from a variety of cactus, in Acajou gum, from *Anacardium occidentale*, and in gum tragacanth, which is obtained from various kinds of astralagus, the gum either exuding of itself or after excision.

It is gathered principally in Asia Minor, Syria, Armenia, Kurdistan, and Persia, and has been known from early times. Theophrastus was acquainted with it, and Dioscorides correctly states that it is derived from a low thorny bush.

Gum tragacanth occurs in commerce in yellowish-white, translucent, flat pieces, which usually exhibit on the surface rounded protuberances, and this variety is known as leaf or sheet gum tragacanth, whilst the so-called worm gum tragacanth forms more or less thick, vermicular masses.

In addition to bassorin, it contains arabin, starch, cellular tissue, and the same mineral constituents as gum arabic. If it be steeped in water, it swells up to a gelatinous mass occupying many hundred times the bulk of the original substance. If it be allowed to increase from 1,000 to 1,200 times the bulk, and the liquid be poured off, the mass, on prolonged agitation with a large quantity of water, becomes thin and fluid, so that it will pass through a filter; in this way the starch and the cellular tissue are kept back, and each drop as it comes through forms a thread. When gum tragacanth is boiled with dilute alkalis

[1] Thomson, *Journ. Prakt. Chem.* [2], xix. 146.
[2] *Monatsch. Chem.* iii. 406.

it forms a substance resembling gum arabic, whilst boiling with dilute acids transforms it into a crystallizable sugar.

In early times the old Greek and Arabian physicians made use of gum tragacanth; it is now employed in pharmacy, and in confectionery, and it is also made use of in the place of other gummy matters in finishing and calico-printing, and also used by shoemakers.

According to the receipt of Gahn the so-called "Sprengkohle" used for leading a crack in glass-working is prepared as follows: A solution of 2·5 parts of gum arabic in 4 parts of water is mixed with the mucilage got by treating 1 part of gum tragacanth with 8 parts of boiling water; a solution of 0·5 parts gum benzoin and 0·5 parts storax is rubbed up in the smallest possible quantity of alcohol, and the whole is intimately mixed with from 6 to 7 parts of very finely powdered wood charcoal, and moulded into rods about 20 cm. long, and of the thickness of an ordinary lead-pencil.

870 *Vegetable mucilage.* Parts of many plants give, on soaking in cold or hot water, a mucilaginous liquid. According to Schmidt, the purified dry substance has the composition $C_6H_{10}O_5$,[1] but Tollens and Kirchner do not find this to be the case with every variety of vegetable mucilage.

*Linseed mucilage* is obtained, by addition of hydrochloric acid and precipitation with alcohol, as a powder which when dried at 100° has the above composition. On prolonged boiling with dilute sulphuric acid it yields a gum and a sugar, both of which are strongly dextro-rotatory, and 4 per cent. of a residue is left resembling cellulose.

The mucilage obtained from the willow weed (*Plantago psyllium*) has the composition $C_{36}H_{58}O_{29}$, and yields more sugar than that from linseed, and it gives 6·3 per cent. of residue.

*Quince mucilage* forms, after purification with hydrochloric acid, alcohol, and ether, a porous mass having the formula $C_{18}H_{28}O_{14}$. With water it yields a gelatinous mass, which is transformed, on addition of a little caustic potash solution, into a mucilage. On boiling with dilute sulphuric acid, it yields a dextro-rotatory sugar, a lævo-rotatory gum, and 34 per cent. of cellulose.

Kirchner and Tollens believe that the mucilages are compounds of cellulose or another similar body with gum, and that the latter, by the action of the acid, is in part converted

[1] *Ann. Chem. Pharm.* li. 29. [2] *Ib.* clxxv. 205.

into sugar, the quantity of which is increased on prolonged boiling.

Other vegetable mucilages, which, like those already described, are used for a variety of purposes in the arts, and especially in pharmacy, occur in marshmallow root (*Althæa officinalis*), in salep (the roots of various orchids), in Irish-moss or rock-moss, a species of seaweed (*Chondrus crispus*), which is found on the rocky coasts of Europe from the North Cape to Gibraltar, and on the east coast of North America. It is not only used in medicine, but also for clarifying beer, in finishing textiles, as fodder, &c.

## CELLULOSE, $(C_6H_{10}O_5)_n$.

871 This compound occurs universally distributed throughout the vegetable kingdom, forming cell membrane, but it is very seldom found pure, inasmuch as other substances pass from the cells into the membrane, and there become fixed. It is built up from soluble carbohydrates contained in protoplasm, and, with the exception of the very young cellular tissue, always contains mineral matters. Cotton-wool, frequently washed linen, and Swedish filter-paper consist of almost pure cellulose; the last-named may be obtained free from ash by treatment with dilute hydrofluoric acid.[1]

It is often of great importance in the paper manufacture, and for other technical purposes, to separate the cellulose from the raw fibre, and determine its quantity. For this purpose Hugo Müller recommends the following method as being the best. Two grams of the substance are dried at 110°—115°; if much wax or resin be present this is extracted by a mixture of benzene and strong alcohol, and then the material is boiled out a few times with water or very dilute ammonia. The substance, squeezed as dry as possible, is next digested with 100 cbc. of water, and from 5 to 100 cbc. of bromine water containing 4 grams of bromine per liter. As soon as the colour of the bromine disappears, more bromine water is added, and this addition is continued until after standing for twenty-four hours the mixture contains free bromine. The substance is then washed with water and heated with a mixture of 2 cbc.

[1] Fellenberg, *Jahresb.* 1854, 648.

of ammonia and 500 cbc. of water almost to the boiling point, again washed, and this successive treatment with bromine and ammonia repeated until the liquid ceases to be coloured brown. Even straw and shavings when thus treated yield a mass of isolated cells resembling paper-pulp, which when washed with water and boiling alcohol assumes a lustrous white appearance.

Cellulose is insoluble in the ordinary solvents, but it dissolves in an ammoniacal solution of cupric oxide. This reaction was discovered by Schweitzer,[1] and the reagent is best prepared by first precipitating with caustic soda a solution of sulphate of copper to which sal-ammoniac has been added, preserving the precipitate under water, and, when the reagent is needed, adding the hydrated cupric oxide to ammonia so long as it dissolves. The deep blue solution dissolves cotton-wool freely.[2] The mucilaginous fluid may be filtered after dilution. On addition of an acid, the cellulose is precipitated as a gelatinous mass resembling alumina, and on drying forms a horny, brownish-grey mass.

Cellulose resists the action of most reagents; thus it is not attacked in the cold by a mixture of potassium chlorate and dilute nitric acid, which soon destroys most other organic bodies. It is thus possible to purify crude cellulose,[3] though the use of bromine water is preferable. Chlorine or bleaching powder destroys it, however, after some time. For this reason paper sometimes becomes friable when the pulp, bleached with chlorine, has not been thoroughly washed. Ozone and hydrogen dioxide in presence of water act similarly, as indeed do certain metallic oxides, though in less degree Thus the injury done to linen by rust stains is well known. A similar slow deterioration in the strength of the fibre takes place in paper and cloth of pure cellulose after lapse of years by the action of the air. A remarkable decomposition of cellulose is that caused by a ferment contained in sewage deposit, and also present in all fertile soil, by which cellulose is decomposed into carbon dioxide and marsh gas.[4] This fermentive decomposition of cellulose must play an important part in the destruction of woody fibre on those portions of the earth's surfaces where the range of temperature is such as to permit its action.

[1] *Jahresb.* 1857, 247. [2] Neubauer, *Fresenius' Zeitschr.* xiv. 196.
[3] Schulze, *Jahresb.* 1857, 491.
[4] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* xvi 122; H. Jappeiner, *ib.* xvi. 1734.

872 *Humus.* As forming intermediate links in the chain from cellulose to the two products above mentioned, come the brown or black substances to which the name of humus has been given, found in vegetable mould, peat, and rotten wood. These bodies, or similar ones, are produced when carbohydrates are acted upon by mineral acids or by alkalis: they are insoluble in acids, but dissolve in alkalis.[1]

*Hydrocellulose.* When cellulose is brought into sulphuric acid of specific gravity 1·42, or into hydrochloric acid of specific gravity 1·16, it undergoes scarcely any visible alteration, but after a time it becomes friable, being converted into *hydrocellulose*, $C_{12}H_{22}O_{11}$, a body likewise obtained by the action of the gaseous hydracids of chlorine, bromine, and iodine on cellulose. This substance is also formed when cellulose is moistened with any dilute mineral acid and then dried. It is soluble in warm potash-lye, and is easily oxidized, absorbing oxygen at as low a temperature as 50°.[2]

This last reaction is employed for the purpose of removing the cotton fibre from mixed goods, the wool, which is unacted upon, being worked up for shoddy.

Cellulose dissolves in concentrated sulphuric acid, an acid termed cellulose-sulphuric acid being said to be formed, though Fehling states that this is a mixture.[3] If this solution be diluted with water and boiled, dextrine and dextrose are formed.[4] Hence sugar, and therefore alcohol, can be prepared from rags or sawdust.

873 *Amyloid* and *Parchment Paper.* Cellulose also dissolves in chlorsulphuric acid, the same products being formed as from dextrose. If 1 part of cotton-wool be dissolved in a mixture of 24 parts of sulphuric acid and 6 parts of water, a gelatinous precipitate of *amyloid* is thrown down on addition of more water. This body forms the outer covering of the well known *parchment paper* now so largely used in place of animal membranes.[5] According to Gaine, parchment paper is best prepared by dipping unsized paper for a few seconds into a cold mixture of two volumes of sulphuric acid

[1] Mulder, *Ann. Chem. Pharm.* xxvi. 243; Peligot, *ib.* xxx. 79; Stein, *ib.* xxx. 84; Gregory, *Ann. Chem. Pharm.* lxi. 365; Berzelius, *Pogg. Ann.* xxix. 3 and 238; Lefort, *Bull. Soc. Chim.* [2], viii. 373; Detmer, *Amer. Chem.* iii. 302; Thénard, *Comp. Rend.* lxxxiii. 375.

[2] Girard, *Bull. Soc. Chim.* xxvi. 190; xxxiv. 407.

[3] *Ann. Chem. Pharm.* liii. 135.

[4] Beehamp, *ib.* c. 367.

[5] Ferwer, *Jahresb.* 1861, 933.

and one volume of water, and then washing first with water, then with dilute ammonia, and lastly, again with water.[1] Parchment paper can also be made by dipping paper into a concentrated solution of zinc chloride.[2]

Amyloid, like starch, is coloured blue by iodine, but the colour disappears soon by the action of water. A reagent by which the cellulose of plants is coloured blue consists of a solution of zinc chloride, of specific gravity 1·8, to 100 cbc. of which six grams of potassium iodide and as much iodine as will dissolve has been added. Cellulose is distinguished from starch by its solubility in Schweitzer's reagent in which starch does not dissolve. Silk also dissolves in the above-named reagent and also in an ammoniacal solution of nickel oxide, which does not act upon cellulose, but this latter body is not attacked by dilute acids, which easily dissolve both wool and silk. If a piece of mixed goods is moistened with dilute hydrochloric acid and then allowed to dry, the woollen and silk fibres are not attacked, whereas the cotton-thread is disintegrated. Cotton-wool heated with concentrated potash to 160° dissolves, and the solution on acidulation yields a precipitate which possesses the composition of cellulose, but is readily soluble in alkalies. Concentrated caustic-lye also acts in the cold on cotton-wool, contracting and thickening the fibres. If caustic soda-lye of a strength not less than specific gravity 1·342 be used, a compound $C_{12}H_{10}O_{10} + NaOH$, is formed, and caustic potash yields a similar compound; both these are decomposed by carbon dioxide.[3]

## Ethereal Salts of Cellulose.

874 *Nitrates of Cellulose* or *Gun-Cotton.* Pelouze was the first to observe, in 1838, that when concentrated nitric acid is allowed to act upon starch-flour, paper, linen, or cotton-wool, the cellulose is converted into an explosive substance which he supposed to be identical with Braconnot's xyloidin, and this view was generally accepted until Schönbein, in 1846, announced his discovery of an explosive cotton which could be used instead of gunpowder, and which was analysed by Walter Crum.[4] Schönbein kept his process secret, but it was soon discovered by Böttger and Otto,

[1] *Jahresb.* 1858, 668.
[2] Taylor, *Journ. Soc. Arts*, 1859, 351.
[3] Gladstone, *Chem. Soc. Journ.* v. 17.
[4] *Phil. Mag.* [3], xxix. 426.

and published by the last-named chemist, who prepared gun-cotton by dipping cotton-wool into the strongest nitric acid and washing the product with water. The publication of the process led many chemists and a still larger number of amateurs to experiment with this remarkable substance.[1]

*Manufacture.* Knop showed that a mixture of sulphuric and nitric acids answered better than the latter acid alone, and the new explosive was manufactured on a large scale, but the results were not satisfactory, inasmuch as the product could not be kept for any length of time, and decomposed sometimes slowly and sometimes so rapidly as to give rise to violent explosions. Thus, on July 17, 1848, a frightful explosion of 16,000 kilos. of gun-cotton took place at Bouchet in France, walls of one metre in thickness being pulverised and heavy objects projected to great distances,[2] whilst similar explosions occurred at Faversham and other places. The manufacture of gun-cotton was, in consequence, almost entirely abandoned, and few had the temerity to believe that it had a future as an explosive. Of these few one was the Austrian artillery general, von Lenk, and another, Sir Frederick Abel, chemist to the English War Office. It is to the perseverance and ability of these two gentlemen, who worked independently of one another, that we owe the discovery of a process by which a perfectly unalterable gun-cotton of constant composition can be prepared, and a powerful explosive is obtained which is far less dangerous to handle than gunpowder.

In the first place, the cotton-wool must be thoroughly freed from fatty or waxy matter by treatment with alkali. Lenk dips the loosely-spun cotton yarn into a boiling dilute solution of carbonate of potash, washes well with water, and dries. Then he brings it into 300 times its weight of a mixture of 1 part of nitric acid of specific gravity 1·485 and 3 parts of sulphuric acid of specific gravity 1·84, allows it to remain in for a few minutes, then takes it out, presses it, and throws it into another similar mixture of acids where it is allowed to remain for forty-eight hours. It is then squeezed out and well washed in running water, dipped into a boiling solution of carbonate of potash, and again washed with water.[3] Further important improvements

[1] For the literature of the subject see Schönbein, "On the Discovery of Gun-cotton," *Phil. Mag.* [3], xxxi. 7; also *Jahresb.* 1847 and 1849, p. 1128; *Journ. Prakt. Chem.* xl. 193; *Pogg. Ann.* lxx. 320.

[2] *Comptes Rend.* xxviii. 345.

[3] "Report on the Application of Gun-cotton to Warlike Purposes," *Brit. Assoc. Reports*, 1863, p. 1; and on p. 8, "System of Manufacture of Gun-cotton as

in the manufacture of gun-cotton were made by Abel. His process consists in bringing the purified, well-dried, unspun cotton-wool into a mixture of 10 parts of a mixture of 1 part of nitric acid of specific gravity 1·5 and 3 parts sulphuric acid of specific gravity 1·85, and leaving it twenty-four hours in contact with the acid. After washing, the wool is placed in a washing engine, such as is used in paper manufacture, and the pulped and washed mass pressed into cylinders.[1]

875 *Properties.* The formula for gun-cotton thus prepared is $C_{12}H_{14}(NO_3)_6O_{10}$, or a hexnitrate of cellulose. This was first ascertained by Walter Crum.[2] The gun-cotton prepared from raw cotton is scarcely to be distinguished from this latter substance in appearance, though it has rather a rougher touch; it becomes powerfully electric on rubbing, crackling and phosphorescing, and emitting sparks in the dark. It does not yield the reaction for amyloid with iodine, and is insoluble in Schweitzer's reagent. On ignition it burns very rapidly, and, unlike powder, leaves no residue. Abel's gun-cotton may be burnt on the hand without scorching the skin, and when placed on some gunpowder it may be fired without igniting the powder. Lenk's cotton does not burn so quietly, and when pressed or tightly spun it burns more slowly. Abel's compressed gun-cotton burns quietly on ignition with a large flame. It remains unaltered in contact with water, and as it is not explosive when wet, it can be preserved or worked in this state without danger. A gun-cotton cartridge, well moistened throughout its mass, may have a hole bored through it with a red-hot iron with as little danger as a piece of wood. To prove the harmless nature of wet gun-cotton the War Department made the following experiment: Two massive erections of stone were built, and in each of these was placed a ton of the moist compressed gun-cotton on iron plates; the buildings were filled with combustible materials, which were then fired. After lapse of a couple of hours the fire had burnt out, the two iron plates were found to be bent by the heat, but no explosion whatever occurred, for the gun-cotton, having been gradually dried, burnt quietly.

carried on in the Imperial Austrian Establishment," by F. A. Abel, *Brit. Assoc. Reports*, 1863.

[1] *Chem. News*, xxiv. 241; see also Abel, *Chem. News*, ix. 254, 268, 284; and Abel, "Contributions to the History of Explosive Agents," *Phil. Trans.* 1866, 269; 1867, 181; 1869, 489; 1874, 337.

[2] *Phil Mag.* [3], xxx. 426.

Gun-cotton explodes on percussion, and the more readily the more it has been previously compressed, but the explosion is much more violent when it is induced by a detonation of fulminating mercury. To give an idea of the force of such an explosion it may be sufficient to state that 120 grams (4 ounces) of compressed gun-cotton fired with a detonating fuse (Abel's) against an ordinary steel railway rail breaks it to pieces. Certain of the old martello towers built on the south coast near Rye, with walls 2 to 3·7 metres thick, were utterly destroyed by exploding 200 pounds of gun-cotton as described. Abel has proved, by means of a chronoscope, that the rate of propagation of the detonation in the interior of a mass of compressed gun-cotton takes place at the rate of 5,200 to 5,900 metres per second. Moist gun-cotton may be made to explode even more violently than the dry material. For this purpose a hole is bored in the centre of the moist cartridge, and this filled with dry gun-cotton, and in the centre of this is placed a fulminating fuse. Gun-cotton is largely used for filling torpedoes, but it is not so much employed for shells, as, owing to the fact that it burns without smoke, the spot at which the shell bursts cannot be seen at a distance; nor has it been largely applied for gunnery purposes in place of gunpowder. It is, however, to use the expression of the Royal Commission which was appointed to investigate the subject, a powerful, reliable, safe, portable, and convenient explosive, especially valuable for submarine operations.

Gun-cotton is also useful in the laboratory for filtering solutions of potassium permanganate or other strongly oxidizing liquids.

The products of combustion of gun-cotton, as is the case with those of gunpowder, differ both in quality and quantity according to the conditions under which it is fired. They consist of nitrogen, nitric oxide, carbon monoxide, carbon dioxide, marsh gas and other hydrocarbons, and aqueous vapour, but when ignited under pressure they contain no nitric oxide, but free hydrogen is present.[1] Cyanogen and hydrocyanic acid have also been detected.[2] This last product occurs together with nitrogen trioxide only when the gun-cotton is burnt slowly under diminished pressure (Abel).

Although properly prepared gun-cotton may be preserved for

[1] v. Károlyi, *Pogg. Ann.* cxviii. 544; Abel, *Proc. Roy. Soc.* xiii. 204.
[2] Porrett and Teschemacher, *Mem. Chem. Soc.* iii. 258; Fordos and Gélis, *Comp. Rend.* xiii. 982.

years both in the dry and in the moist state without undergoing deterioration, the material, if containing even a trace of free acid, decomposes on standing with a greater or less degree of rapidity, red nitrous fumes and carbon dioxide being given off, and formic and oxalic acids, together with other products, being produced.[1] Large masses of insufficiently washed gun-cotton when stored may evolve heat enough on decomposition to bring about an explosion. Such an explosion occurred at Stowmarket in 1871, and on investigation it was ascertained that some of the stock of gun-cotton contained acid, owing either to insufficient washing or to the felonious addition of acid to the properly washed gun-cotton.

876 *Collodion.* Soon after the discovery of gun-cotton, Messrs Maynard and Begelow, as well as MM. Ménard and Domonte,[2] observed that this body, prepared by a certain process, dissolves in a mixture of alcohol and ether, and it was not long before this solution was employed in America for a variety of purposes. It was then proved that the hexnitrate is insoluble in the above reagents, whilst the lower nitrates dissolve. These latter are obtained by allowing the acid to act on the cotton fibre for a shorter time, and by the above-mentioned reaction may be separated from the hexnitrate, which is insoluble in a mixture of ether and alcohol, methyl alcohol, glacial acetic acid, and ethyl acetate, but forms a jelly with acetone, and dissolves in a large volume of this liquid.[3]

When cotton-wool is treated with mixed acids only for a few minutes, the *tetranitrate*, $C_{12}H_{16}(NO_3)_4O_{10}$, and the *trinitrate*, $C_{12}H_{17}(NO_3)_3O_{10}$, are formed; the action of somewhat less concentrated acids for a longer period producing the same result. These compounds dissolve in a mixture of alcohol and ether, in methyl alcohol, and in acetic ether. The trinitrate also dissolves slowly in absolute alcohol, whilst the tetranitrate does not; it is, however, not possible in this way to effect a complete separation of the two compounds (Eder).

*Cellulose Dinitrate*, $C_{12}H_{18}(NO_3)_2O_{10}$, is formed as the first product of the action of the hot dilute mixture of acids upon cotton-wool, or as the last product of the action of caustic potash or ammonia on the alcoholic and ethereal solution of the higher

[1] Hofmann, *Jour. Chem. Soc.* xiii. 76, 282; Bonet, *Comp. Rend.* liii. 405; Luca, *ib.* liii. 298.

[2] *Compt. Rend*, xxiv. 390.

[3] Eder, *Ber. Deutsch. Chem. Ges.* xiii. 169, where an account of the literature of the subject from 1862 is to be found.

nitrates. It is a flocculent powder or a transparent gum-like mass, easily soluble in the above-named solvents with the exception of pure ether. It also dissolves in caustic potash-lye, but this solution readily undergoes decomposition with production of a brown, gummy mass, the mononitrate not being formed. According to Girard, hydrocellulose yields a very explosive hexnitrate, soluble in ether-alcohol.

The application of the sensitised collodion film to photographic purposes was made by Scott Archer, with whom Dr. Hugh Diamond was associated in 1851.

The following is the method of making pyroxyline prescribed by Hardwich, who was the first to thoroughly investigate the manufacture of pyroxyline fit for the manufacture of collodion:

A mixture of

500 cbc. of sulphuric acid, sp. gr. 1·842
166·6 cbc. of nitric acid, sp. gr. 1·456
145·7 cbc. of water

is made by mixing the nitric acid and water, and afterwards adding the sulphuric acid. The temperature is then allowed to cool to 65°, and a dozen balls of cleaned and dried cotton-wool, each weighing about 1·5 gram, separately immersed in the liquid, and, after thoroughly soaking, allowed to remain at the bottom of the vessel. This immersion should be rapidly carried out, otherwise decomposition may take place, and the whole of the cotton may dissolve with the evolution of nitrous fumes. The balls must be left in the acid from ten minutes to a quarter of an hour, and they are then ready for washing, which must be completely done, best in running water. Several other formulæ have been given for the preparation of pyroxyline, and many recipes for making collodion, differing in the relative quantity of alcohol and ether used as a solvent. Hardwich uses 12 to 14 grams of pyroxyline, and 450 cbc. of alcohol, specific gravity 0·82, and 550 cbc. of ether, specific gravity 0·725.[1]

The chief use of collodion is for preparing sensitive photographic films, but it is also used in surgery, for making small balloons, &c.

All the nitrates of cellulose give up nitric acid when treated with alkalis, and concentrated sulphuric acid displaces the nitric acid almost completely even in the cold. The nitrates are also converted into cellulose by the action of reducing agents such as

[1] For further information consult Abney's *Treatise on Photography*, Longmans.

ferrous acetate, potassium hydrosulphide, or a solution of stannous oxide in caustic soda. The same change occurs when the nitrate is boiled with ferrous sulphate and hydrochloric acid, the whole of the nitrogen escaping as nitric oxide, air being excluded, and this reaction can be used as a ready means of determining the amount of nitration of a pyroxylin (Eder).

$$C_{12}H_{14}(NO_3)_6O_{10} + 30HCl + 30FeSO_4 = C_{12}H_{20}O_{10} + 12H_2O + 6NO + 10Fe_2(SO_4)_3 + 5Fe_2Cl_6.$$

*Acetates of Cellulose.* When filter-paper or cotton-wool is heated to 180° with six to eight times its weight of acetic anhydride, cellulose hexacetate, $C_{20}H_{14}(C_2H_3O_2)_6O_{10}$, is formed; this compound separating out as a white, flocculent mass on addition of water. It is soluble in glacial acetic acid, being precipitated by alkalis as structureless cellulose. If a smaller amount of acetic anhydride is employed, lower acetates are formed.

## Woody Fibre or Lignin.

877 During the processes of plant-growth certain of the cell membranes retain their primitive composition, whilst others undergo a change known as lignification. The tissue thus becomes hard, woody, and less tough, but does not lose its power of permeability to liquids. The substance thus formed, termed lignin, has not yet been obtained in the pure state.[1] It forms about half the weight of ordinary wood, and as we know the composition of wood, and can ascertain the relative amounts of cellulose and lignin which wood contains, it is possible to arrive at the composition of lignin. Schulze has proposed the formula $C_{19}H_{24}O_{10}$,[2] but Sachsse gives the formula $C_{18}H_{24}O_{10}$.[3] As wood does not give, like cellulose, the amyloid reaction, and does not dissolve in Schweitzer's solution, it has been assumed that the cellulose and lignin are combined together in the woody fibre, and for this supposed compound the name of lignose has been proposed.

According to Erdmann, pine-wood (*Pinus abies*) consists of *glucolignose*, $C_{30}H_{46}O_{21}$, which can be obtained pure by extracting the finely rasped wood with very dilute acetic acid, hot water,

[1] Payen, *Compt. Rend.* viii. 51; xlviii. 210.
[2] *Chem. Centralbl.* 1857, 321.
[3] *Chem. Farbstoffe, Kohlenhydrate*, &c.

alcohol, and ether. The yellowish-white residue yields traces of cellulose when treated with cupric-oxide-ammonia. When boiled with dilute hydrochloric acid, grape sugar is formed and glucolignose remains.

$$C_{30}H_{46}O_{21} + 2H_2O = C_{18}H_{26}O_{11} + 2C_6H_{12}O_6.$$

Glucolignose does not dissolve in Schweitzer's reagent, but, when boiled with very dilute nitric acid, cellulose is formed, together with other bodies not yet investigated, but which probably belong to the aromatic series.[1] Hence Erdmann considers glucolignose to be an ether of lignose containing together with the cellulose group a sugar-forming and an aromatic group. Bente has confirmed the above composition for pine-wood, and shown that the same substance exists in the wood of the poplar, but differs from Erdmann as to the proportion of grape-sugar formed.[2] Singer, who has also investigated this subject, has arrived at the conclusion that lignin is a mixture of various compounds.[3] Jute fibre has been subjected to careful examination by Bevan and Cross,[4] who have shown that, together with about 70 to 72 per cent. of cellulose, it contains a considerable quantity of an incrusting substance belonging to the aromatic series of compounds. Runge observed many years ago that pine-wood was stained yellow by aniline in presence of an acid, and Hofmann found that salts of other amido-bases act in a similar way. Wiesner next pointed out that the process of lignification can be detected by this reaction, and that aniline sulphate, now generally used in micro-chemical work, serves best for this purpose. A more delicate reagent for lignified tissue, accordingly to Wiesner, is phloro-glucin, $C_6H_6O_3$, a compound which frequently occurs in the vegetable kingdom, and which gives rise to an intense red colour when the tissue is moistened with a 5 per cent. solution and afterwards with hydrochloric acid.[5] If phenol, $C_6H_6O$, be employed instead of phloro-glucin, the lignified tissue becomes bluish-green or bright blue on exposure to sunlight, and especially when dried.[6] According to Singer, all these colorations are produced by aromatic substances contained in the wood.

[1] Julius Eadmann, *Ann. Chem. Pharm.* Suppl. v. 223.
[2] *Ber. Deutsch. Chem. Ges.* viii. 476.
[3] *Monatsch. d. Chem.* iii. 395.
[4] *Chemical News*, xlii. 77, 91 ; xliv. 64 ; *Journ. Chem. Soc.* 1883, i. 18.
[5] Dingler, *Polyt. Journ.* ccxxvii. 397.
[6] v. Höhnel, *Sitzungsb. Wien. Akad.* 1877, 39.

878 *Cork or Cuticular Substances.* The process of cuticularization takes place on the outer cells or those lying near the surface, which thus become more elastic and more difficultly penetrated by gases, as well as water and other liquids. Cork is formed by the continued formation of such cells, and is found in largest quantities in the outer bark of the *Quercus suber*, the cork tree growing to the height of thirty or forty feet in the south of Europe, Africa, and the East. In addition to this modified form of cellulose which constitutes the greatest part of the cork, a waxy and resinous mass termed suberine is present which can be dissolved out by alcohol and ether, and which can be obtained in the crystalline form.[1] Analysis shows that this substance belongs to the aromatic series, but it has not been more closely examined. Cork contains more carbon and more hydrogen than lignin, and in addition some nitrogen. On oxidation with nitric acid, cork yields oxalic, suberic, and azelaic acids. In order to make corks air-tight, it is usual to plunge them, after drying, into melted paraffin, and thus treated they resist the action of chlorine and acids more perfectly.

The following words of Liebig point out the value of cork to the chemist:[2] "What precious properties are conbined in cork! How little can any but chemists appreciate its value and recognize its good qualities. We might rack our brains in vain in the hope of replacing cork, as the ordinary means of closing bottles, by any other substance whatever. Let us imagine a soft, highly elastic mass which Nature herself has inpregnated with a matter having properties resembling wax, tallow, resin, yet dissimilar to all these and termed suberine. This renders it perfectly impermeable to fluids and even to gases."

### The Technical Uses of Cellulose.

879 The most important uses of cellulose in the arts and manufactures are for spinning and weaving and for paper making. Cotton-wool has been employed from the earliest times for the manufacture of textile fabrics in all those countries in both hemispheres where the cotton plant is indigenous, and at the present time the cotton plant is largely grown throughout the world in a zone limited to thirty-six degrees of

[1] Chévreul, *Ann. Chem.* xcvi. 170; Döpping, *Ann. Chem. Pharm.* xlv. 290; Siebert, *Journ. Prack. Chem.* civ. 1181.

[2] *Familiar Letters of Chemistry*, p. 124.

north and of south latitude. The cotton plant of commercial importance is of two typical kinds, the Indian or Oriental (*Gossypium herbaceum*), and the American or Occidental (*G. barbadence* and *G. hirsutum*). The cultivated cotton is naturally perennial, or has become so. The cotton is contained in the pod or boll, which is filled with a mass of fine fibre surrounding the seeds. The value of the cotton depends on the length of its staple, as well as on its silky nature. The Sea Island cotton has a staple which is 40·5 mms. in length, and ·025 mm. in width, while the Bengal or Surat cotton is only 18 mms. in length, and ·019 mm. in width. Cotton fibre consists of a long, hollow, cylindrical, perfectly-closed cell, thickest at the root end, where attached to the seed, and tapering off at the other end. This regular form is but seldom seen under the microscope, the cells usually presenting the appearance of irregularly twisted ribbon with thick rounded edges, as shown in Fig. 148. This form is retained in the manufactured thread, and hence cotton cloth is distinguished from that made from other fibres by its loose woolly structure, this imparting to it the property of being a bad conductor of heat, as well as giving it an opaque character. Figs. 150 and 151 show a cross section of the fibre after drying. Cotton can be more readily dyed than most vegetable fibre, and hence its use as a basis of printed goods. This property, according to Walter Crum, depends upon its peculiar structure. In order that cotton shall take up colour, the latter must be soluble, and pass by diffusion into the interior of the cell, where it is rendered insoluble by chemical means. Unripe cotton fibre frequently contained in the wool cannot be dyed, and is therefore termed "dead cotton." These defective fibres are very thin and transparent, and solid throughout the mass, Figs. 149 and 152.[1] The dyeing power of the cotton fibre is increased after treatment with concentrated caustic soda, the alkali combining with the cellulose, the effect being to shrink the fibre, as shown in Fig. 153. This process, termed from its inventor mercerizing, has not been much employed owing to its cost.[2]

Raw cotton, even when quite white, contains a small quantity of other materials than cellulose. These, according to Schunck, are characteristic of the plant, and among them are found a wax, solid fatty acids, pectic acid, albuminoid substances and colouring

[1] *Phil. Mag.* 3rd Series, vol. xxxv. 334.
[2] Mercer, *British Assoc. Rep.* 1851, 157.

matters, one of which is easily soluble, and the other only slightly soluble in alcohol. Coloured cotton, as that of Nankin, contains the same constituents in larger quantity.[1]

FIG. 148.

FIG. 149.

*Flax and Hemp.*—After cotton the most important fibres are flax and hemp. Flax fibre (*Linum usitatissimum*) was used as a

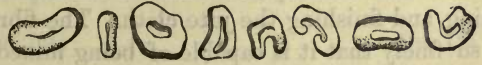


FIG. 150.

material for textiles in the earliest times, as may be seen from the Egyptian mummy cloths, which do not contain a single

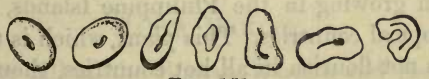


FIG. 151.

fibre of cotton. Some of these being so fine that twenty metres

[1] *Memoirs Manchest, Phil. Lit. Soc.* 1868.

of thread weigh only one gramme,[1] and a hundred hanks go to the pound, the cloth having 140 threads in the inch in the warp, and about 64 in the woof. Both flax and hemp plants (*Cannabis sativa*) must be subjected to a process of "retting," or modified fermentation or rotting, and this is accomplished by "water retting," or "dew retting" or "snow retting." In all cases the fermentation takes place, this having for its purpose the decomposition of the intercellular mass, so as to enable the fibre to be separated by mechanical means. Many plans have been proposed to avoid this tedious rotting process, but none as yet have been successful, though a maceration in warm water has been adopted in some works, as reducing the time of fermentation. So long ago as the year 1678 Leuwenhœk showed that cotton fibre could be easily distinguished from that of flax (Fig. 154) under the microscope, as the latter consists of cylindrical fibres open at each end, containing knots. Hemp (Fig. 155) has a similar structure, the fibre, however, being thicker.

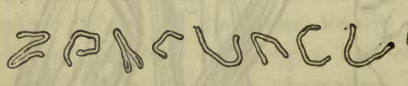


Fig. 152.

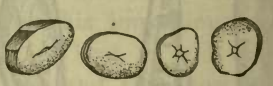


Fig. 153.

*Jute.* Jute is the fibre of two species of *Corchorus*, viz. *capsularis* and *olitorius*, growing in India, and especially in Bengal, and only recently imported into European markets, though it appears to have been used from early times in India as well as in Egypt and Syria. The jute fibre possesses a silky lustre, can be easily dyed, but is not so strong as flax. Considerable advances have lately been made both in its manufacture and its dyeing, and finishing the jute cloth. The fibres can now be divided so finely that it is capable of being mixed with silk, though the main use of jute is in making bags, sacks, and other rougher articles. Jute fibre is coloured a deeper yellow by aniline sulphate than any other fibre.

*Manilla Hemp.* This is the fibre of the *Musa textilis*, or the wild plantain growing in the Philippine Islands, Borneo, Java, and other tropical countries. This plant, which is the non-edible banana, does not flourish in all hot countries, though the edible banana grows luxuriously throughout the tropics. The leaf-

[1] James Thompson, "On the Mummy Cloth of Egypt, with some Observations of the Manufactures of the Ancients," *Phil. Mag.* 1834, 355; also *Ann. Chem. Pharm.* lxix. 128.

stalks of the plant are used for the preparation of the fibre, 3,200 trees producing about one ton. Manilla hemp is almost exclusively used for rope making, as the fibre is much stronger and lighter than ordinary hemp.

*Bleaching.* Yarn as well as woven cloth has always a greyish colour, and is obliged to be bleached before it can be used for many purposes. This process was formerly carried on in bleach greens, the ozonized atmospheric oxygen produced by the action of the sunlight being the active agent. Bleaching powder is now usually employed for this purpose on the large scale [1] for cotton

FIG. 154.

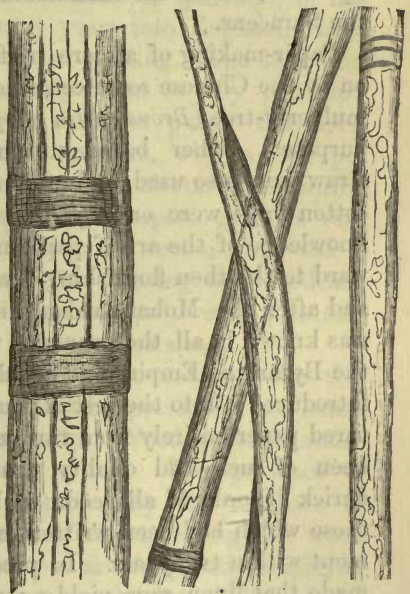


FIG. 155.

goods, though linen is still chiefly bleached on the green. (For a description of the theory of bleaching and of the manufacture of bleaching powder, see Vol. I. p. 266, Vol. II. Part I. p. 200.)

## PAPER MAKING.

880 With the fall of the Roman Empire and the consequent decline of European civilization, the use of Egyptian papyrus,

[1] See art. "Bleaching," Spon's *Encyclop. of Industrial Arts*, by Hummel; see likewise an article on the materials used in textile industries, by Hugo Müller, *Ber. Entwicklung. Chem. Indust.* vol. ii. 32.

which was employed as a writing material, diminished, and the manufacture, which had been chiefly carried on at Alexandria, soon ceased.

For preparing the material, the pith of the *Papyrus antiquorum*, a bulrush growing on the Nile, was cut into thin plates, laid lengthways alongside one another, with their edges touching, while another layer was laid across at right angles. On moistening with warm water and pressing, the films were made to adhere, and the layers became a compact sheet. At the present day paper from papyrus is made as a curiosity in Syracuse, where the manufacture was originally introduced by the Saracens.

Paper-making of a more perfect kind was, however, carried on by the Chinese some centuries before our era, the bark of a mulberry-tree (*Broussonetia papyrifera*) being employed for this purpose. Other barks, cotton fibres, and various kinds of straw were also used, and after about a century, old linen and cotton rags were employed as paper-making materials. The knowledge of the art of paper-making spread from China westward to the then flourishing towns of Samarcand and Bokhara, and after the Mohammedan conquests of Central Asia, paper was known in all the countries which they overran, and also in the Byzantine Empire and Southern Spain, whilst the Crusaders introduced it into the rest of Europe. The Arabians manufactured paper entirely from raw cotton, but this appears to have been of such bad quality that in 1221 the Emperor Frederick II. ordered all deeds to be written on parchment, and those which had been written on paper to be copied on parchment within two years. In process of time the discovery was made that linen rags yield a much stronger and more permanent paper, so that this material has since this time been chiefly used for paper-making. But in the eighteenth century this material could not be obtained in sufficient quantity to keep pace with the demand for paper, and hence attempts were made to obtain a convenient substitute. It appears to have been forgotten that in China a number of vegetable fibres had long ago been used for paper-making, and it was not until the beginning of the present century that Matthias Koops[1] succeeded in manufacturing a paper from straw and wood, which, though it possessed a yellow colour, was strong and of a very

[1] *Invention of Paper: an Historical Account of Substances which have been Used to Describe Events and Convey Ideas*, London, 1800.

permanent character.[1] The preliminary treatment which straw fibre has to undergo before it can be made into white paper, is, however, of an expensive character, and the demand for paper increasing enormously, the manufacturers sought for a material which could be more easily worked up than straw. This was found in the esparto-grass (*Macrochloa tenacissima*), which grows wild over large tracts on the coast of Spain, and on the north coast of Africa from Mogador to Egypt. Though this material was used from the earliest times by the natives for the manufacture of ropes, mats, &c., and is even mentioned by the Roman writers under the name of *spartium*, it has only been introduced within recent years into England, where it is now very largely used for paper making. The long thin leaves of this plant yield from forty-seven to fifty per cent. of their weight in paper, and in order to purify the fibre, these are boiled, generally under pressure, with a two per cent. soda lye, and, after washing, manufactured according to the ordinary methods. The fibre of esparto-grass is very opaque, standing in this respect next to the cotton fibre, and it yields a paper specially well suited for printing fine woodcuts. It is, however, usual to mix the esparto-pulp with a certain quantity of pulp from cotton or linen rags, or straw.

*Wood pulp* is largely employed in paper-making. For this purpose a certain length of fibre must be preserved, and hence the wood is rubbed up into a fine pulp. Wood paper is somewhat brittle, and never perfectly white. The presence of lignified tissue can readily be detected by the sulphate of aniline test (see p. 584). Instead of disintegrating the wood by mechanical means, chemical agents are frequently employed for obtaining the cellulose, sawdust or shavings being heated under considerable pressure with caustic soda. In this way a soft mass of cellulose is obtained, which, when further disintegrated, yields a valuable pulp. Several other methods have been proposed for converting wood or straw into paper pulp. One of these consists in macerating the disintegrated material for twelve hours with dilute milk of lime, and then saturating the mixture with sulphur dioxide gas, under a pressure of from four to five atmospheres; after next washing the pulp for two hours with water, it is treated under pressure with

[1] Accum's *System of Theoretical and Practical Chemistry*, published by the Author in 1803, was printed on paper made from straw, which at the present time is in as good condition as the day it was printed.

a three per cent. solution of calcium chloride, or with one containing 0·5 per cent. of aluminium sulphate, and these again removed by washing. In paper-making from rags the first operation is that of cutting, effected either by hand or machine. The rags are then passed through a machine termed the devil, or thrasher, by which the rags are still further disintegrated. They are then boiled with caustic alkali to remove any grease they may contain, and afterwards passed through the washing and rag engine, termed a Hollander, because it was invented by the Dutch. This engine contains a rotating cylinder, making about 230 revolutions per minute, and is filled with water and the rags, fresh water being constantly brought in and the dirty water escaping. All the engines through which the rags pass up to this state are termed breakers, and the pulp is known as *half stuff*. The next process is that of bleaching, which is effected either by chlorine gas or by bleaching powder, or by both of these agents combined.

After the pulp has been bleached by either of these methods the chlorine must be removed by careful washing, the apparatus employed being called a beating-engine. As the complete removal of chlorine by mere washing is a tedious process, the addition to the bleached pulp of a so-called *anti-chlor* is often resorted to. The commonest forms of anti-chlor are sodium thiosulphate (hyposulphite of soda of the shops) and sodium sulphite, both these bodies are oxidized to sulphates by free chlorine (Vol. II. Part II. p. 118). The pulp is then ready to be brought on to the paper-machine.[1]

*Japanese paper*, distinguished by its peculiar tenacity, is manufactured from the long fibres of the bark of the paper mulberry-tree, whilst the so-called *rice-paper* of the Chinese is not prepared from rice, but from the snow-white pith of *Araliapapyrifera*, a small shrub only found now in the marshy forests of Formosa.

881 *The technical uses of wood* are generally so well known as scarcely to require enumeration. In chemical technology it is employed for the preparation of wood spirit, pyroligneous acid, &c., by subjecting it to dry distillation in retorts, when wood-charcoal is left and gases evolved, whilst the water containing the above-named substances distils over with wood-tar. The composition of the latter varies with the kind of wood employed.

[1] For a complete account of processes of paper-making, see Carl Hofmann, *Practical Treatise on Paper-making*, Philadelphia, 1873.

Thus, beech-wood tar is distinguished by the amount of creosote, a mixture of phenol and its methyl ethers, substances belonging to the aromatic series, which it yields, whilst birch-wood tar possesses a peculiar smell, and is used in the preparation of Russian leather. The use of wood in the preparation of wood-spirit and of oxalic acid have already been mentioned.

*Preservation of Wood.* Whilst pure cellulose is a very stable body, wood, when placed in moist earth, moulders or rots, on account of its containing nitrogenous constituents, which give rise to minute organisms favouring the process of decay. In early times surface carbonization was found to exert a protective influence, and this was long made use of; but at the beginning of this century numerous proposals were made to prevent the rotting of the wood by means of chemical antiseptics. In 1821 Davy and Knowles proposed the use of corrosive sublimate for this purpose, and this suggestion was successfully carried out by Kyan in 1832. Railway-sleepers are now impregnated with heavy tar-oils, or with zinc chloride, as a means of preventing decay. For this purpose the dried sleepers are heated in air-tight boilers, from which the air is pumped out, and then the antiseptic liquid is allowed to flow in, by which means a perfect impregnation of the wood by the liquid is effected.[1]

## TUNICIN $(C_6H_{10}O_5)_n$.

882 This substance, also known as vegetable cellulose, is found in the mantle of ascidia.[2] In order to prepare it, the mantle is heated in a Papin's digester, then treated for some time with hydrochloric acid, and, after washing with water, boiled for some days with strong caustic potash, and then washed, first with water and finally with alcohol.[3]

Tunicin retains the outward form of the mantle, and is a thin translucent mass. Like cellulose, it gives the amyloid reaction, and dissolves in Schweitzer's reagent.

Concentrated nitric acid converts it into an explosive nitrate, but it remains unaltered after boiling for some weeks with

[1] For a complete account of the chemical and technical properties and uses of vegetable fibres, see Hugo Müller's article in the second volume of Hofmann's *Bericht über Fortschritte der chemischen Industrie.*

[2] C. Schmidt, *Ann. Chem. Pharm.* lviii. 318; Löwig and Kölliker, *Journ. Prakt. Chem.* xxxvii. 439.

[3] Schäfer, *Ann. Chem. Pharm.* clx. 312.

dilute acids. It dissolves, however, in concentrated sulphuric acid, and this solution boiled with water gives dextrose.[1] Schmidt considers tunicin to be identical with vegetable cellulose, but according to Berthelot, who gave to it its name, tunicin is distinguishable by the fact that it withstands the action of acids more completely, and that it is not coloured by fluoride of boron in the cold, whilst cellulose is turned black.[2] Schäfer, however, is of Schmidt's opinion, whilst Berthelot adheres to his own.[3] According to Luca, the skin of the silk-worm,[4] as well as that of the snake,[5] contains cellulose, convertible on boiling with dilute sulphuric acid into glucose; and Virchow[6] found a similar cellulose-like body in the human brain and in the diseased spleen.

## PECTOUS SUBSTANCES.

883 If the juice of ripe fruit, such as apples and pears, or that of fleshy roots, such as carrots, beets, &c., be boiled in order to remove albuminoid substances, and if then alcohol be added to the liquid, a gelatinous substance is precipitated, which can also be obtained from the bark of trees. This body, to which Braconnot[7] gave the name of pectin (πηκτός, curdled), as well as the compounds, some of which are acid bodies, which are readily formed from it, have been examined by other chemists, especially by Chodnew[8] and Frémy.[9] These chemists, however, have not obtained concordant results, as the former gives for pectin the formula $C_{28}H_{42}O_{24}$, whilst Frémy gives $C_{16}H_{24}O_{16}$. According to the latter chemist, an insoluble compound termed pectose occurs in fleshy roots and unripe fruit, and imparts to them their hardness, and this in the process of ripening, or on boiling with acids, is converted into pectin. According to Städe, pectose is a lime compound of pectin.[10] Other gelatinous bodies are formed by the action of alkalis, the last product of which, according to Frémy, is metapectic acid, $C_8H_{14}O_{19}$, a body which can easily be obtained by treating the root with milk of lime.[11] Scheibler, however, finds that this body is identical with arabic acid, being formed

[1] Franchimont, *Ber. Deutsch. Chem. Ges.* xii. 1938.
[2] *Ann. Chim. Phys.* [3], lvi. 149.
[3] *Bull. Soc. Chim.* [2], xviii. 9.
[4] *Jahresb.* 1861, 721.
[5] *Ibid.* 1863, 651.
[6] *Ibid.* 1853, 592.
[7] *Ann. Chim. Phys.* l. 376.
[8] *Ann. Chem. Pharm.* li. 355.
[9] *Ann. Chim. Phys.* [3], xxiv. 9.
[10] *Ann. Chem. Pharm.* cxxxi. 244.
[11] *Compt. Rend.* xlix. 561.

from the metarabin contained in beetroot.[1] It is, however, probably formed from the parabin which Reichardt found to exist in beetroot, and which probably is one of the pectous substances described by Frémy. Hence it would appear that the latter body must be placed amongst the gums.

## DIBASIC ACIDS, $C_6H_{10}O_8$.

884 *Saccharic Acid.* This name was first applied by Scheele[2] to an acid which he obtained by the oxidation of cane-sugar with nitric acid, and which he afterwards found to be ordinary oxalic acid. In 1785 he observed that, together with this, another acid occurred, which he considered to be malic acid. In 1830 Trommsdorff pointed out that this is not the case,[3] and Guérin Varry, who arrived at the same conclusion, termed the new acid "*acide oxalhydrique*," as in his opinion it might be regarded as a compound of oxalic acid and hydrogen.[4] Erdmann considered it to be an isomeride of tartaric acid, and therefore termed it metatartaric acid,[5] whilst Hess, in 1837, correctly determined its constitution and gave to it Scheele's original name of saccharic acid.[6] It was afterwards further examined by Thaulow,[7] Liebig,[8] and Heintz.[9] It is produced by the action of nitric acid, not only upon sugar, but also upon mannite, dextrose, lævulose, trehalose, melizitose, dextrin, lævulin, starch, and milk-sugar. The last named yields at the same time the isomeric mucic acid.

For the preparation of saccharic acid 2 parts of sugar are heated with 7 parts of nitric acid of specific gravity 1·27 until an evolution of gas sets in, whereupon the mixture is allowed to cool down to 60° and maintained at this temperature until it begins to turn brown. The solution is next slightly diluted with water and removed from the separated oxalic acid; it is then neutralized with potassium carbonate, and acetic acid added until the liquid smells strongly of the acid. On standing for some weeks, or it may be months, crystals of the acid potassium salt separate out. From the mother-liquor a further crop of

[1] *Ber. Deutsch. Chem. Ges.* vi. 612.
[2] *Opusc.* ii. 203.
[3] *Ann. Pharm.* xxx. 36.
[4] *Ann. Pharm.* xxx. 24.
[5] *Journ. Prakt. Chem.* ix. 257.
[6] *Ann. Pharm.* xxvi. 1; xxx. 302.
[7] *Ib.* xxvii. 113.
[8] *Ib.* xxx. 313; xxxiii. 117; cxiii. 4.
[9] *Journ. Prakt. Chem.* lxxiv. 474; lxxvi. 246; lxxxi. 134.

the crystals is obtained on evaporation, but these are mixed with potassium oxalate. To remove the latter the mixed salts are dissolved in warm water containing acetic acid, the solution precipitated with calcium chloride, the filtrate supersaturated with ammonia, and then evaporated. The calcium salt thus obtained is next transformed into the acid potassium salt, and this is purified by recrystallization. This is then converted into the normal salt and the solution precipitated by a salt of cadmium. The well-washed precipitate is decomposed by sulphuretted hydrogen, and the filtrate evaporated on the water-bath. The residue on drying in a vacuum over sulphuric acid forms a brittle amorphous mass, which becomes sticky in the air. It is readily soluble in water and alcohol and possesses a strongly acid taste. On further oxidation with nitric acid it yields first tartaric acid together with a smaller quantity of racemic acid (Hornemann):

$$\begin{matrix} CH(OH).CH(OH).CO_2H \\ | \\ CH(OH).CH(OH).CO_2H \end{matrix} + 2O =$$

$$\begin{matrix} CH(OH).CO_2H \\ | \\ CH(OH).CO_2H \end{matrix} + 2CO_2 + 2H_2O.$$

Saccharic acid reduces ammoniacal silver solution with deposition of a metallic mirror. When heated with phosphorus and hydriodic acid to 140°—150° it yields adipic acid $C_4H_8(CO_2H)_2$, together with other products.

*Saccharates.* The normal alkali salts are deliquescent, whilst the acid salts are but slightly soluble in water and crystallize well. *Acid Potassium Saccharate,* $C_6H_9KO_8$, forms rhombic crystals, soluble at 7° in 89 parts of water. *Normal Calcium Saccharate,* $C_6H_8CaO_8 + H_2O$, forms a flocculent precipitate, which from hot water crystallizes in rhombic microscopic prisms; these are scarcely soluble in boiling water, but dissolve readily in a solution of the free acid. *Normal Cadmium Saccharate,* $C_6H_8CdO_8$, separates from a cold solution in flocculæ which are difficult to wash; whilst from a boiling solution of the potassium salt it is precipitated by cadmium sulphate in the form of miscroscopic needles. *Lead Saccharate,* $C_6H_8PbO_8$, is obtained as a curdy precipitate when sugar of lead is added to a boiling solution of the potassium salt containing acetic acid. If the precipitation

be effected in neutral solution, the hydrogen of the whole of the hydroxyl is replaced by lead, and the salt $C_6H_4Pb_3O_8$ is obtained, and this was formerly considered to indicate that saccharic acid was hexabasic.

*Ethyl Saccharate*, $C_6H_8(C_2H_5)_2O_8$. When hydrochloric acid is passed into a mixture of calcium saccharate and alcohol, rhombic prisms of the compound $2C_6H_8(C_2H_5)_2O_8 + CaCl_2$ are formed, and these are decomposed by boiling water with formation of alcohol and saccharic acid. If, however, they be dissolved in a small quantity of cold water, the solution precipitated with sodium sulphate and alcohol, and then evaporated in a vacuum, ethyl saccharate remains behind. This may be extracted with a mixture of alcohol and ether, and on evaporating the solution the compound remains as a crystalline mass possessing a bitter taste. If the calcium chloride compound be treated in the cold with acetyl chloride, the acetate, $C_6H_4(C_2H_3O)_4(C_2H_5)_2O_8$, is obtained, and this crystallizes from hot alcohol in tables which melt at 61°.[1]

*Saccharamide*, $C_4H_4(OH)_4(CO.NH_2)_2$, is an amorphous powder, obtained by passing ammonia into an ethereal solution of ethyl saccharate. It is soluble in water, and on boiling its solution is transformed into ammonium saccharate.

## Mucic Acid.

885 This compound, which is isomeric with saccharic acid, was first prepared in 1780 by Scheele, who obtained it together with oxalic acid by the action of nitric acid on milk-sugar. In 1785 he found that this acid, which he termed *acidum saccharilactis* or *acidum galactosaccharinum*, may also be obtained from gum tragacanth, whilst Fourçroy and Vauquelin pointed out that it may likewise be obtained from other kinds of gums and mucilages, and hence they termed it *acide muqucux*, which name was afterwards changed to *acide mucique*. In addition to the above compounds, it is also obtained by the oxidation of dulcite, melitose, and galactose, which, as we know, is formed together with dextrose by the action of acids on milk-sugar; this latter being, therefore, the only carbohydrate which yields at the same time both mucic and saccharic acids.

[1] Baltzer, *Ann. Chem. Pharm.* cxlix. 241.

Mucic acid was first more closely examined by Malaguti[1] and by Pelouze and Liebig.[2]

For its preparation, 1 part of milk-sugar and 4 parts of common nitric acid are warmed together, when a violent evolution of red vapours takes place. When this has ceased, the mixture is boiled for a short time, and, after cooling, the separated mucic acid is filtered off. A further quantity is obtained from the mother-liquor on evaporation.[3]

Mucic acid forms a pulverulent crystalline powder, consisting of oblique rhombic prisms. It is difficultly soluble in cold, but dissolves more readily in hot water, and it is insoluble in alcohol. On further oxidation with nitric acid it is first converted into racemic acid (Hornemann), and on heating with phosphorus and hydriodic acid it forms some adipic acid.[4]

*Mucates.* These salts are distinguished from the saccharates by the fact that their normal alkali salts are less soluble in water than the corresponding acid salts, which crystallize well. The salts of the other metals are either insoluble or slightly soluble. They have been examined by Malaguti, Hagen, and Johnson. When mucic acid is boiled with sugar of lead, the salt, $C_6H_4Pb_3O_8$, is formed.

*Ethyl Mucate*, $C_6H_8(C_2H_5)_2O_8$, was obtained by Malaguti by warming together 1 part of mucic acid and 4 parts of sulphuric acid until the liquid began to blacken, and then, after standing twelve hours, adding 4 parts of alcohol of specific gravity 0·814. The crystals which separated after standing for twenty-four hours were then purified by recrystallization. Ethyl mucate is not formed by the action of hydrochloric acid on a mixture of mucic acid and alcohol (Limpricht). It crystallizes in four-sided prisms, which melt at 158° with decomposition, and is readily soluble in boiling water and alcohol. It dissolves at 20° in 44 parts of water, whilst at 15°·5 it requires for solution 156 parts of alcohol of specific gravity 0·814.

When heated with acetyl chloride to 100°, the acetate, $C_6H_4(C_2H_3O)_4(C_2H_5)_2O_8$, is formed, and this crystallizes from boiling alcohol in needles, which melt at 177°.[5]

*Ethyl Mucic Acid*, $C_6H_9(C_2H_5)O_8$, is obtained by the decomposition of the impure normal salt (Malaguti), or when the pure

[1] *Ann. Chim. Phys.* [2], lx. 195 ; lxiii. 131.
[2] *Ann. Pharm.* xix. 258 ; xxvi. 160 ; cxiii. 1.
[3] Schwanert, *ib.* cxvi. 265 ; see also Limpricht, *ib.* clxv. 253.
[4] Crum-Brown, *Ann. Chem. Pharm.* cxxv. 19.
[5] Werigo, *Ann. Chem. Pharm.* cxxix. 195.

compound is boiled with water (Limpricht). It is readily soluble in water and alcohol, and crystallizes in lustrous needles, containing three molecules of water of crystallization, which melt below 100° to a glassy hygroscopic mass.

*Mucamide*, $C_4H_4(OH)_4(CO.NH_2)_2$, is produced by the action of ammonia on the ethyl salt. It is somewhat soluble in boiling water, and crystallizes from this solution in microscopic rhombic pyramids or tables, which do not dissolve either in alcohol or ether.[1]

885 *Paramucic Acid* was obtained by Laugier by evaporating a solution of mucic acid in boiling water.[2] In order to purify it the residue is dissolved in alcohol and allowed to evaporate spontaneously.[3] It forms crystalline crusts composed of rectangular tables. Its taste is more strongly acid than that of mucic acid, and it also dissolves more readily in water than the latter acid. It is again converted into mucic acid when it is attempted to recrystallize it from hot water. The salts of paramucic acid (with the exception of the normal ammonium salt) dissolve more readily in water than those of mucic acid, into which latter they are converted on boiling with water.

When mucic acid is treated with phosphorus pentachloride the following reaction takes place :[4]

$$C_4H_4(OH)_4(CO.OH)_2 + 6PCl_5 =$$
$$C_4H_2Cl_2(COCl)_2 + 6POCl_3 + 8HCl.$$

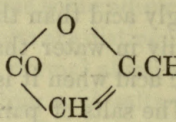
The same chloride is also formed in a corresponding way from acid potassium saccharate.[5] From its solution in carbon disulphide it separates in large crystals.[6] It is decomposed by water with formation of *chlormuconic acid*, $C_4H_2Cl_2(CO.OH)_2$, and from boiling water this latter acid crystallizes in long white needles. On heating with alcoholic potash it is decomposed with formation of oxalic and acetic acids (Limpricht).

By the action of sodium amalgam and water it is transformed into *hydromuconic acid*, $C_4H_6(CO_2H)_2$, which crystallizes from hot water in long needles, melting at 195°. If, however, an excess of sodium amalgam be employed, adipic acid

[1] Malaguti, *Compt. Rend.* xxii. 854.
[2] *Ann. Chim.* lxxii. 81.
[3] Malaguti, *Ann. Chim. Phys.* lx. 197.
[4] Liès-Bordat, *Ann. Chem. Pharm.* c. 325 ; Bode, *ib.* cxxxii. 95.
[5] Bell, *Ber. Deutsch. Chem. Ges.* xii. 1274 ; De la Motte, *ib.* xii. 1571.
[6] Wichelhaus, *Ann. Chem. Pharm.* cxxxv. 250.

$C_4H_8(CO_2H)_2$, is produced. Hydromuconic acid unites with bromine to form *dibromadipic acid*, $C_4H_6Br_2(CO_2H)_2$, which crystallizes in needles, and by the action of silver oxide on the hot aqueous solution of the last-named acid, it is transformed into *muconic acid*, $C_6H_6O_4$. This is a monobasic acid, and it forms large crystals which exhibit numerous faces, and probably belong to the monoclinic system. It melts at a little above 100°, and on boiling with baryta-water decomposes into acetic acid, succinic acid, carbon dioxide, and another acid which has not been further examined.

Muconic acid is monobasic and homologous with aconic acid. From its products of decomposition it may be assumed that its constitution is probably the following:



887 *Dehydromucic Acid*, $C_4H_2O(CO_2H)_2$, is formed in smaller quantity, together with pyromucic acid, $C_4H_3O(CO_2H)$, by the dry distillation of mucic acid.[1] A better yield is obtained by heating mucic acid with hydrochloric acid,[2] or with hydrobromic acid.[3] According to Klinkhardt it may be prepared in largest quantity when equal parts of mucic acid, fuming hydrochloric acid, and concentrated hydrobromic acid are heated together for eight hours to 150°. In this reaction other products are also formed, amongst which are carbon dioxide and diphenylene oxide, $C_{12}H_8O$, a compound belonging to the aromatic group:

$$4C_6H_{10}O_8 = C_6H_4O_5 + C_{12}H_8O + 6CO_2 + 14H_2O.$$

Dehydromucic acid dissolves but slightly in cold water; it is more readily soluble in hot water, and crystallizes from this solution in lustrous needles or laminæ, which may be sublimed by careful heating. If, however, the acid be quickly heated, it decomposes into carbon dioxide and pyromucic acid. When its aqueous solution is shaken up with bromine water, it is transformed into fumaric acid, carbon dioxide being evolved:

$$C_5H_4O_3 + 3H_2O + 3Br_2 = C_4H_4O_4 + 2CO_2 + 6HBr.$$

[1] Klinkhardt, *Journ. Prakt. Chem.* [2], xxv. 41.
[2] Heinzelmann, *Lieb. Ann.* cxciii. 187.
[3] Seelig, *Ber. Deutsch. Chem. Ges.* xii. 1081.

It is a strong dibasic acid, forming salts which crystallize well. It is a characteristic reaction that its aqueous solution on addition of ferric chloride quickly solidifies to a transparent gelatinous mass.

By the action of sodium amalgam and water it yields two isomeric acids, $C_4H_4O(CO_2H)_2$, which may be separated from one another by taking advantage of the different solubilities of their barium salts. The one of these acids crystallizes in thin tablets, which are easily soluble in water and alcohol, and melt at 144°. The other acid forms large hard crystals, which contain one molecule of water, this being given off on heating. The anhydrous acid melts at 173° (Seelig).

## FURFURYL GROUP.

888 *Furfurol*, or *Furfuraldehyde*, $C_4H_3O.COH$, was first prepared by Döbereiner, who obtained it, together with formic acid, by the distillation of sugar with dilute sulphuric acid and manganese dioxide, and he termed it artificial oil of ants.[1]

Stenhouse then found that this compound is also produced when flour or sawdust is distilled with dilute sulphuric acid, and he ascertained its composition.[2] It was observed by Fownes that this substance may be got in largest quantity from bran, and on this account he termed the oily liquid, furfurol (*furfur*, bran, and *oleum*, oil).[3]

It is also formed when bran is distilled with a concentrated solution of zinc chloride,[4] or when, in the preparation of garancin, madder is boiled with dilute sulphuric acid.[5] Further, it is produced, together with other products, when wood is heated with water to 198°.[6] It is found in fusel oil,[7] in the distillation-products of sugar and of wood,[8] being present in especially large quantity if the latter be not heated above 200°.

*Preparation.* Furfurol is best obtained from bran, which contains a peculiar substance giving elasticity to the husk of the grain.[9] This is soluble in potash lye and in boiling dilute sulphuric acid; and in the latter solution it is at first transformed into a saccharine substance, which on distillation yields furfurol.[10]

To prepare furfurol, one part of bran is mixed with an equal quantity of sulphuric acid and three parts of water, and distilled until three parts have passed over. The distillate is

[1] *Schweigg. Journ.* lxiii. 368.
[2] *Phil. Mag.* xviii. 122; xxxvii. 226.
[3] *Phil. Trans.* 1845, 253.
[4] Babo, *Ann. Chem. Pharm.* lxxxv. 100.
[5] Stenhouse, *ib.* clvi. 197.
[6] Greville Williams, *Chem. News*, xxvi. 231, 293.
[7] Förster, *Ber. Deutsch. Chem. Ges.* xv. 230; Jorissen, *ib.* 574.
[8] Völckel, *Ann. Chem. Pharm.* lxxxv. 65; lxxxvi. 66.
[9] Heill, *Ber. Deutsch. Chem. Ges.* x. 936.
[10] Gudkow, *Zeitsch. Chem.* 1870, 360.

neutralized with carbonate of soda, and after addition of common salt, one half of the liquid is distilled off, and then rectified, in which operation the furfurol passes over first mixed with water. To purify the product, it is treated with very dilute sulphuric acid, and from time to time potassium dichromate is added in very small quantities; it is then dried over calcium chloride and after this distilled.[1] The yield amounts to about three per cent. of the bran taken.

Furfurol is an oily liquid which has a smell resembling at the same time both bitter almond oil, and oil of cinnamon, but less pleasant than these, whilst in taste it resembles the last-named oil. It boils at 161° and has a specific gravity at 13°·5 of 1·1636. It is soluble in 12 parts of water, and dissolves readily in alcohol. When exposed to the air it darkens in colour and finally is transformed into a tarry mass. Like other aldehydes it unites with acid sodium sulphite, forming a compound which crystallizes in scales.[2] Silver oxide oxidizes it to pyromucic acid,[3] which latter is also formed, together with furfuryl alcohol, by the action of alcoholic potash on furfurol:[4]

$$2C_5H_4O_2 + KOH = C_5H_3KO_3 + C_5H_6O_2.$$

889 *Furfuryl Alcohol*, $C_4H_3O.CH_2.OH$, which is also formed by the action of sodium amalgam and water on furfurol,[5] has not yet been prepared in the pure state, as on heating, it for the most part loses water and is changed to a resinous mass, this transformation also occurring when it is attempted to distil it in a vacuum or in a current of hydrogen. On keeping, it passes into a pasty mass, whilst acids at once transform it into a red resinous body.

*Furfuramide*, $(C_4H_3O.CH)_3N_2$, is formed by the action of aqueous ammonia on furfurol, and for its preparation the aqueous distillate obtained in making furfurol may conveniently be employed. It is insoluble in cold water and crystallizes from alcohol in thin needles, which melt at 117°. When treated with acids, it decomposes into ammonia and furfurol.

*Furfurin* is an isomeride of furfuramide and is obtained by adding the latter body to a boiling solution of caustic potash,[6] or by heating it alone to 110°—120°.[7]

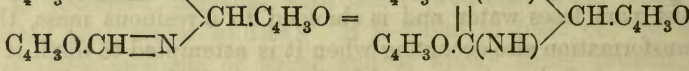
[1] Stenhouse, *Ann. Chem. Pharm.* clvi. 198.
[2] Schwanert, *Ann. Chem. Pharm.* cxvi. 258.
[3] Schwanert, *ib.* 257.
[4] Ulrich, *Zeitsch. Chem.* 1861, 186; Limpricht, *Ann. Chem. Pharm.* clxv. 279.
[5] Beilstein and Schmelz, *Ann. Chem. Pharm.* Suppl. iii. 275.
[6] Fownes, *Phil. Trans.* 1845, 253; *Ann. Chem. Pharm.* liv. 55.
[7] Bertagnini, *ib.* lxxxviii. 128.

To purify the product it is dissolved in a boiling solution of an excess of oxalic acid, in order to obtain the acid oxalate which is difficultly soluble in cold water. The boiling solution of this salt is then decolorized with animal charcoal and afterwards decomposed by ammonia. Furfurin dissolves in 4,800 parts of cold, and in 135 parts of boiling water, crystallizing out on cooling in small rhombic prisms which melt at 116°.[1] It dissolves readily in alcohol and ether, possesses an alkaline reaction, and is a monacid base whose salts crystallize well.[2]

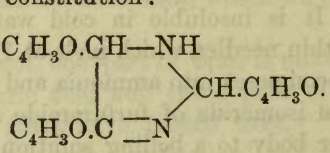
When heated with ethyl iodide it yields *ethyl furfurin*, $C_{15}H_{11}(C_2H_5)N_2O_3$, which, when the resulting iodide is decomposed with silver oxide and the solution evaporated, remains behind as a syrup.[3] When furfurin is warmed with acetic anhydride it is transformed into *acetyl furfurin*, $C_{15}H_{11}(C_2H_3O)N_2O_3$, which forms a crystalline mass insoluble in water, and not attacked by either ethyl iodide or nitrogen trioxide (R. Schiff).

By mixing very dilute solutions of furfurin sulphate and potassium nitrite, *nitroso-furfurin*, $C_{15}H_{11}(NO)N_2O_3$, is obtained, which yields crystals melting at 112°.[4]

Furfurin is an imido-base, and is probably produced from furfuramide in the following way:



According to this formula it would contain two imido-groups, whilst its derivates only indicate the existence of one such group. But it may here be pointed out that in diethyl-urea only one atom of hydrogen of the two imido-groups can be replaced by nitroxyl. It is, however, possible that furfurin has the following constitution:



890 *Condensation products of Furfurol.* From the above description of the compounds of furfurol it will be seen that this

[1] R. Schiff, *Ber. Deutsch. Chem. Ges.* x. 1186.
[2] Swanberg and Bergstrand, *Journ. Prakt. Chem.* lxvi. 229.
[3] Davidson, *Edin. New. Phil. Mag.* (1855) ii. 284.
[4] R. Schiff, *Ber. Deutsch. Chem. Ges.* xi. 1250.

body bears a striking resemblance to the aldehyde of benzoic acid which constitutes the principal constituent of bitter almond oil. Like this latter substance, it yields condensation products, and these have been examined by E. Fischer, who has given them names analogous to those of the well-known derivatives of benzoic aldehyde.[1]

*Furoïn*, $C_{10}H_8O_3$, is produced by boiling furfurol with dilute alcohol and potassium cyanide. It crystallizes from hot water in fine prisms, which melt at 135°, and dissolve in caustic soda solution yielding a deeply coloured dark-red liquid, which by reflected light has a bluish-green colour. This solution becomes colourless in the air from the formation of furil. When boiled with acetic anhydride, *acetyl-furoïn*, $C_{10}H_7(C_2H_3O)O_3$, is produced, and this crystallizes from hot water in needles melting at 76°—77°.

The following equation explains the formation of furoïn:

$$\begin{matrix} C_4H_3O.COH \\ | \\ C_4H_3O.COH \end{matrix} = \begin{matrix} C_4H_3O.CO \\ | \\ C_4H_3O.CH.OH \end{matrix}$$

*Furil*, $C_{10}H_6O_4$, is formed when a current of air is passed through a solution of furoïn in dilute alcohol:

$$\begin{matrix} C_4H_3O.CO \\ | \\ C_4H_3O.CH.OH \end{matrix} + O = \begin{matrix} C_4H_3O.CO \\ | \\ C_4H_3O.CO \end{matrix} + H_2O.$$

It is almost insoluble in water and crystallizes from hot alcohol in golden yellow needles which melt at 162°. It unites with bromine to form *furil octobromide*, $C_{10}H_6Br_8O_4$, which yields yellow crystals, and on heating is transformed into *dibromfuril*, $C_{10}H_4Br_2O_4$. This last-named body crystallizes from hot alcohol in golden yellow laminæ, which melt at 183°—184°, and sublime without decomposition.

### Pyromucic Acid, $C_4H_3O.CO_2H$.

891 Scheele observed in 1780, that when mucic acid is heated it yields an acid sublimate, the vapour of which possesses a penetrating odour, resembling that of benzoic or succinic acid. Trommsdorff assumed that acetic, pyrotartaric and succinic acids are thus formed, but Houton-Labillardière showed that the sublimed acid is a new compound. The dry distillation of mucic acid is not a method which can be recom-

[1] *Ann. Chem. Pharm.* ccxi. 214.

mended for the preparation of pyromucic acid, as by-products are formed, and consequently the yield of the acid is small. If furfurol be oxidized with silver oxide, about 14 per cent. of the theoretical quantity of the acid is formed, whereas if alcoholic caustic potash be employed the yield amounts to 33 per cent. Hence in order to prepare this acid, furfurol is mixed with a rather dilute solution of alcoholic potash, and the mixture repeatedly exhausted with ether to remove furfuryl alcohol. The potassium pyromucate is then dissolved in a small quantity of water, a resin being left behind. The filtrate is next heated with hydrochloric acid, when white pyromucic acid separates out on standing for twenty-four hours, whilst that remaining in solution is obtained by shaking up with ether (Limpricht).

Pyromucic acid dissolves in 28 parts of water at 15° and in 4 parts at the boiling point; it crystallizes in long plates which melt at 134°, but sublime at 100° in needles.

*The Pyromucates.*[1] The salts of pyromucic acid are nearly all soluble in water, and like the acid itself give a red precipitate with ferric chloride.

*Ethyl Pyromucate,* $C_5H_3O_3(C_2H_5)$, is obtained by the action of hydrochloric acid on an alcoholic solution of the acid.[2] It crystallizes in tables, which melt at 34° and are insoluble in water; it boils at between 208° and 210°, and it is not attacked by acetyl chloride. Ammonia converts it into the amide, $C_4H_3O.CO.NH_2$,[3] which may also be obtained from the chloride $C_4H_3O.COCl$.[4] The last named compound is a pungent-smelling liquid, which has not been prepared in the pure state.[5] The amide forms warty crystals, which easily sublime in tablets resembling those of benzoic acid, and melt at 142°. When distilled with phosphorus pentachloride[6] or phosphorus pentoxide,[7] furfuronitril, $C_4H_3O.CN$, is formed, a liquid smelling like benzonitril and boiling at 147°. By the action of zinc and sulphuric acid it is converted into furfurylamin, $C_4H_3.CH_2.NH_2$. This is a powerfully refracting liquid, smelling like coniin, and boiling at 147°.

892 *Addition Products of Pyromucic Acid.* When the acid is exposed to the vapours of dry bromine, a tetrabromide is formed,

[1] Beilstein and Schmelz, *Ann. Chem. Pharm.* Suppl. iii. 285.
[2] Malaguti, *ib.* xxv. 276; Schiff and Tasssinari, *Ber. Deutsch. Chem. Ges.* xi. 1840. [3] Schwanert, *Ann. Chem. Pharm.* cxvi. 282.
[4] Liès-Bodart, *Compt. Rend.* xlviii. 391.
[5] Limpricht and Rohde, *Ann. Chem. Pharm.* clxv. 280.
[6] Wallach, *Liebig's Ann.* ccxiv. 227, 751.
[7] Ciamician and Dennstedt, *ib.* 1058. [8] Ciamician and Dennstedt, *ib.* 1475.

$C_5H_4Br_4O_3$, which is soluble in cold water and separates in well-formed cystals from its solution in a mixture of ether and petroleum spirit. Reducing agents re-convert it readily into pyromucic acid, whilst chromic acid solution oxidizes it to dibromsuccinic acid. Ethyl pyromucate also combines with four atoms of bromine; the compound separating out from chloroform in colourless crystals, which melt at from 46° to 48° and decompose at a higher temperature, becoming easily reduced again to ethyl pyromucate.[1] The ethereal salt combines also with four atoms of chlorine, when a transparent syrup is obtained having a pleasant smell of the wood of the allspice tree (*Calycanthus floridus*).[2]

When an aqueous solution of pyromucic acid is saturated with chlorine, mucochloric acid is obtained:[3]

$$C_5H_4O_3 + 2H_2O + 4Cl_2 = C_4H_2Cl_2O_3 + CO_2 + 6HCl.$$

It crystallizes from hot water in rhombic tablets, which melt at 125°. Aqueous alkalis decompose it in the cold into formic and *a*-dichloracrylic acid.

By the action of bromine on an aqueous solution of pyromucic acid, a compound is first formed to which Limpricht has given the name of aldehyde of fumaric acid:

$$C_5H_4O_3 + 2Br_2 + 2H_2O = C_4H_4O_3 + CO_2 + 4HBr.$$

This forms a syrup, from which crystals separate on standing. It is a monobasic acid which on oxidation is transformed into fumaric acid;[4] its constitution being, therefore, the following:

$$C_2H_2\begin{cases} COH \\ CO.OH. \end{cases}$$

By the action of an excess of bromine *mucobromic acid*, $C_4H_2Br_2O_3$, is formed, and this crystallizes from hot water in glistening laminæ which melt at 120°.[5] When treated with water and caustic baryta, it yields *β*-dibromacrylic acid and brompropiolic acid.[6] Oxidizing agents transform it into dibrommaleic acid:[7]

$$C_2Br_2\begin{cases} COH \\ CO_2H \end{cases} + O = C_2Br_2\begin{cases} CO_2H \\ CO_2H. \end{cases}$$

[1] Tönnies, *Ber. Deutsch. Chem. Ges.* xi. 1085.
[2] Malaguti, *Ann. Chem. Pharm.* xxv. 279; xxxii. 41.
[3] Schmelz and Beilstein, *ib.* Suppl. iii. 279.
[4] Limpricht, *Ann. Chem. Pharm.* clxv. 285; Baeyer, *Ber. Deutsch. Chem. Ges.* x. 1361.
[5] Beilstein and Schmelz, *Ann. Chem. Pharm.* Suppl. iii. 276; Limpricht, *ib.* clxv. 293.
[6] Hill and Jackson, *Ber. Deutsch. Chem. Ges.* xi. 1671.
[7] Hill, *ib.* xiii. 734.

### Substitution Products of Pyromucic Acid.

893 *Monobrompyromucic Acid*, $C_5H_3BrO_3$. When ethyl pyromucate is combined with two atoms of bromine and the product then treated with alcoholic potash, two acids of the above composition are formed. Of these one forms glistening scales which melt at 180°, and are almost insoluble in cold and dissolve but little in hot water. The second acid is easily soluble and crystallizes in thin needles, which melt between 156° and 157°. When boiled with acidulated water this is gradually transformed into the first-named acid.[1]

*Dibrompyromucic Acid*, $C_5H_2Br_2O_3$, is produced by the action of alcoholic potash on the tetrabromide of pyromucic acid. It crystallizes in small scales which melt at 184°—186°, and sublime at a higher temperature. It is not attacked by a boiling solution of chromic acid, but it dissolves in bromine water with evolution of carbonic dioxide and formation of the aldehyde of mucobromic acid, $C_4H_2Br_2O_2$, a substance readily soluble in water and crystallizing from ether in concentrically grouped needles which melt at 88°. When warmed with chromic acid solution, or if bromine be led into its boiling aqueous solution, it is oxidized to mucobromic acid.[2]

*Sulphopyromucic Acid*, $C_5H_3O_3(SO_3H)$, is obtained by treating pyromucic acid with sulphur trioxide, and yields a barium salt, $(C_5H_3O_3)_2(SO_3)_2Ba$, which does not crystallize well.[3]

*Nitropyromucic Acid*, $C_5H_3(NO_2)O_3$, is produced by the action of a mixture of concentrated nitric and sulphuric acids on dihydromucic acid:

$$C_4H_2O(CO_2H)_2 + NO_2.OH = C_4H_2(NO_2)O.CO_2H + H_2O + CO_2.$$

It is difficultly soluble in water, but dissolves readily in alcohol and crystallizes in transparent, yellow, rectangular prisms or tables which melt at 183°. By the action of tin and hydrochloric acid it is transformed into succinic acid:[4]

$$C_4H_3(NO_2)O.CO_2H + 2H_2 + H_2O = C_2H_4(CO_2H)_2 + CO_2 + NH_3.$$

894 *Tetrol*, $C_4H_4O$. This compound, which is also known as *tetraphenol* or *furfuran*, is produced by heating barium pyromucate

[1] Schiff and Tassinari, *Ber. Deutsch. Chem. Ges.* xi. 842; 1840.
[2] Tönnies, *Ber. Deutsch. Chem. Ges.* xi. 1088; xii. 1202.
[3] Schwanert, *Ann. Chem. Pharm.* cxvi. 268.
[4] Klinkhardt, *Journ. Prakt. Chem.* [2], xxv. 51.

with addition of a little soda-lime. It is a peculiarly-smelling liquid, which boils at 32°, and if a little be allowed to evaporate quickly on a glass rod a portion of it crystallizes. It is not attacked by bromine even on warming, but acids decompose it with formation of pyrrol-red.[1]

Tetrol appears also to be found contained together with *sylvan* or methyl-tetrol, $C_4H_3(CH_3)O$, amongst the distillation products of pine wood. Sylvan is a liquid boiling at 63°. It is not attacked by sodium, whilst hydrochloric acid converts it into a resinous mass. By potassium permanganate it is oxidized to acetic acid.[2]

### Pyrrol, $C_4H_4(NH)$.

895 This compound was found in coal-tar by Runge, who noticed that the smallest quantity of its vapour imparted a deep red colour to a shaving of pine wood, moistened with hydrochloric acid, and on this account he gave the new substance the above name (from πυῤῥός, flame-coloured). By this reaction he also detected its presence in ammonia-water of the gasworks, in the vapours given off in the carbonization of horn and bone, and in the so-called oil of tobacco.[3] He did not, however, succeed in isolating this compound, but this was accomplished by Anderson, who separated it from Dippels-oil and fixed its formula.[4] It is formed in larger quantity, together with other products, in the dry distillation of feathers and of flannel, and likewise of several alkaloids,[5] and it is also produced when the vapour of diethylamine is passed through a tube heated to dull redness:[6]

$$(C_2H_5)_2NH = C_4H_4(NH) + 3H_2.$$

Schwanert then observed that it occurs amongst the products of the dry distillation of ammonium mucate:[7]

$$C_4H_4(OH)_4(CO_2NH_4)_2 = C_4H_5N + CO_3(NH_4)H + CO_2 + 3H_2O.$$

This decomposition proceeds more readily if glycerine be added.[8] Pyrrol is also produced, and in large quantity, in the dry distillation of ammonium saccharate.[9]

Pyrrol is a colourless liquid, which has a pleasant ethereal smell; it boils at 133° and when exposed to the air gradually

[1] Limpricht and Rodhe, *Ann. Chem. Pharm.* clxv. 281.
[2] A. Herberg, *Ber. Deutsch. Chem. Ges.* xiii. 879.
[3] *Pogg. Ann.* xxxi. 67. [4] *Ann. Chem. Pharm.* lxxxiii. 63; cv. 349.
[5] Williams, *Chem. Gaz.* 1858, 309 and 321.
[6] Bell, *Ber. Deutsch. Chem. Ges* x. 1861. [7] *Ann. Chem. Pharm.* cxvi. 278.
[8] Goldschmidt, *Zeitsch. Chem.* 1867. 280.
[9] Bell and Lapper, *Ber. Deutsch. Chem. Ges.* x. 1961.

acquires a brown colour. It is almost insoluble in water, but dissolves slowly in dilute acids, without, however, entering into combination with them. With mercuric chloride, however, it forms a crystalline compound, $C_4H_5N + 2HgCl_2$, which does not dissolve in water. Strong acids decompose pyrrol, with formation of the *pyrrol-red* before mentioned, its production being explained by Anderson as follows:

$$3C_4H_5N + H_2O = C_{12}H_{14}N_2O + NH_3.$$

Pyrrol-red is a light, orange-red powder, which does not dissolve in water, and is but slightly soluble in alcohol.

Pyrrol unites with nascent hydrogen, forming *pyrrolin*, $C_4H_6(NH)$, an oily liquid that boils at 90°—91°, and acts as a strong base.[1]

*Carbopyrrolamide*, $C_5H_6N_2O$. By the dry distillation of ammonium mucate and of mucamide, Malaguti obtained a crystalline body which he termed *pyromucamide biamidée*.[2] Schwanert, who examined this substance more closely, found it to be the amide of carbopyrrolic acid, $C_4H_4N.CO_2H$.[3] For its preparation the aqueous liquid is separated from the pyrrol and evaporated, and the crystals are repeatedly recrystallized from alcohol, the solution previous to the final crystallization being treated with animal charcoal. It forms laminæ which are slightly soluble in water, possess a sweet taste (Malaguti), melt at 176°·5 and decompose at a higher temperature. Ammonium saccharate does not yield any carbopyrrolamide (Bell and Lapper).

*Carbopyrrolic acid*, $C_4H_4N.CO_2H$. The barium salt of this acid is obtained by boiling the amide with baryta solution, and crystallizes in thin, flexible plates. If concentrated hydrochloric acid be added to a cold concentrated solution of the barium salt, the greater part of free acid is precipitated, and this must be quickly separated from the liquid. The residual liquor very quickly becomes rose-red coloured and then brown, and the acid contained in it cannot be separated, as even on most careful evaporation of the solution it is transformed into pyrrol-red with evolution of carbon dioxide.

Carbopyrrolic acid crystallizes from dilute alcohol in small prisms which at 190° sublime, yielding broad feathery crystals. At a slightly higher temperature it is decomposed into carbon dioxide and pyrrol.

[1] Ciamician and Dennstedt, *Ber. Deutsch. Chem. Ges.* xvi. 1536.
[2] *Compt. Rend.* xxii. 856.
[3] *Ann. Chem. Pharm.* cxvi. 270.

896 *Ethyl-pyrrol*, $C_4H_4.NC_2H_5$, is produced in the dry distillation of the mucate and of the saccharate of ethylamine.[1] It is a colourless liquid which in smell resembles pyrrol. It boils at 131° and imparts an intense red colour to a pine shaving moistened with hydrochloric acid. It does not, however, yield any pyrrol-red when heated with hydrochloric acid.

Together with ethyl-pyrrol, ethylamine mucate yields also *diethylcarbopyrrolamide*, $C_5H_4(C_2H_5)_2N_2O$, and *triethyldicarbopyrrolamide*, $C_6H_4(C_2H_5)_3N_3O_2$; but these products are not obtained from the corresponding saccharate. The first-named body crystallizes in prisms which melt at 43°—44°; it boils at 269°—270°, and on heating with alcoholic potash solution splits up into ethylamine and *ethyl-carbopyrrolic acid*, $C_4H_3N(C_2H_5)$-$CO_2H$. This acid crystallizes from hot water in glistening silky needles which melt at 78° and readily decompose into ethyl-pyrrol and carbon dioxide. The triethyldicarbopyrrolamide is a crystalline mass which does not dissolve in water. It melts at 229°—230° and on heating with alcoholic potash to 130° splits up into ethylamine and *ethyl-dicarbopyrrolic acid*, $C_4H_2N(C_2H_5)(CO_2H)_2$. The last named acid crystallizes from alcohol in needles, and when heated to 250° it decomposes, without previously melting, into ethyl-pyrrol and carbon dioxide.

The corresponding methyl and amyl compounds have also been prepared and examined by Bell.

*Acetyl-pyrrol*, $C_4H_4.NC_2H_3O$. By acting on pyrrol with potassium, potassium-pyrrol is produced, and this, when treated with acetyl chloride, yields acetyl-pyrrol. It is a liquid which boils at 177°—178°, has a very peculiar smell, and on heating with potash solution is split up into pyrrol and acetic acid. Acetyl-pyrrol is also formed when pyrrol is heated together with acetic anhydride and anhydrous sodium acetate. The principal product of this reaction is, however, *pseudo-acetyl-pyrrol*, $C_4H_3(C_2H_3O)NH$, a substance which was formerly considered to be acetyl-pyrrol itself.[2] It crystallizes from ether in splendid needles, which melt at 90°; it boils at 220° and is not decomposed by caustic potash solution. If its hot aqueous solution be treated with silver nitrate and a little ammonia, a crystalline precipitate is obtained having the composition $C_4H_3(C_2H_3O)NAg$.[3]

[1] Bell, *Ber. Deutsch. Chem. Ges.* x. 1861; Bell and Lapper, *ib.* x. 1961.
[2] R. Schiff, *Ber. Deutsch. Chem. Ges.* x. 1500.
[3] Ciamician and Dennstedt, *ib.* xvi. 2348.

## Isomerides and Homologues of Pyromucic Acid.

897 *Isopyromucic Acid*, $C_4H_3O.CO_2H$, is formed, together with pyromucic acid, in the dry distillation of ammonium mucate. It is very easily soluble in water, and decomposes carbonates but slowly. It may therefore be separated from pyromucic acid by exhausting the mixture with a small quantity of water, or the distillate may be treated with barium carbonate and then shaken up with ether. This acid melts at 82°, easily sublimes in tablets and yields with iron chloride a deep green colouration.[1]

*Fucusol*, $C_5H_4O_2$. This compound, which is isomeric with furfurol, was obtained by Stenhouse by distilling certain sea algæ (*Fucus*), peat-moss (*Sphagnum*), and lichens (*Usnea*, *Cetraria*, &c.), with dilute sulphuric acid. It is an oil which resembles furfurol; it has a specific gravity of 1·150 at 13°·5, and boils at 171°—172°, a part of the substance being, however, converted into a resin. It differs from furfurol by being somewhat less soluble than this body in water and ammonia, The last-named substance converts it into *fucusamide*, $(C_4H_3O.CH)_3N_2$, which crystallizes from alcohol in long needles; on boiling with a weak solution of caustic potash it is transformed into its isomeride *fucusin*, a substance which at 8° dissolves in 2,400 parts of water, and separates from hot water in flat concentrically grouped crystals. It has an alkaline reaction and forms crystalline salts.[2]

*Fucusoic Acid*, or *β-Pyromucic Acid*, $C_4H_3O.CO_2H$, is formed when fucusol is boiled with silver oxide and water, and crystallizes from aqueous solution in rhombic tables which melt at 130°.[3]

*Furfuracroleïn*, $C_4H_3O.C_2H_2.COH$, is obtained when a mixture of furfurol and aldehyde is warmed with a weak solution of caustic soda:

$$C_4H_3O.COH + CH_3.COH = C_4H_3O.CH \overline{=} CH.COH + H_2O.$$

It crystallizes from hot water in needles which have an odour resembling that of cinnamon. These melt at 51° and by careful heating may be sublimed. When boiled with water and silver oxide[4] it is transformed into the compound next to be described.

[1] Limpricht and Rohde, *Ann. Chem. Pharm.* clxv. 256, 298.
[2] *Ann. Chem. Pharm.* lxxiv. 284.
[3] Stenhouse, *Proc. Roy. Soc.* xx. 80.
[4] J. G. Schmidt, *Ber. Deutsch. Chem. Ges.* xiii. 2342.

898 *Furfuracrylic Acid*, $C_4H_3O.C_2H_2.CO_2H$, is also produced when a mixture of furfurol, acetic anhydride, and anhydrous sodium acetate is heated for some hours to the boiling point:

$$2C_4H_3O.COH + \left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O =$$

$$2C_4H_3O.CH = CH.CO.OH + H_2O.$$

It is difficultly soluble in cold water, and crystallizes from hot water in long brittle needles which resemble cinnamon in smell, melt at 135°, and may be volatilized in a current of aqueous vapour.

This acid is isomeric with salicylic acid. It combines with nascent hydrogen forming furfurpropionic acid, $C_4H_3O.C_2H_4.CO_2H$, which has a strong cinnamon-like smell, and forms crystals which melt at 51°.

If to its aqueous solution one molecule of bromine and afterwards three molecules of silver oxide be added, the silver salt of dibasic *furonic acid*, $C_5H_6O_3(CO_2H)_2$ is formed; this acid crystallizes from hot water in needles which melt at 180°. With nascent hydrogen it unites to form *hydrofuronic acid*, $C_5H_8O_3(CO_2H)_2$, a substance readily soluble in water and crystallizing in needles which melt at 112°. If this acid be heated with hydriodic acid and phosphorus to 200°, it is reduced to *a-pimelic acid*, $C_5H_{10}(CO_2H)_2$.[1]

*Furfurangelic Acid*, $C_4H_3O.C_4H_6.CO_2H$, is formed by heating together furfurol, butyric anhydride, and sodium butyrate. It crystallizes in needles which melt at 88°, and unites with hydrogen forming *furfurvaleric acid*, $C_4H_3O.C_4H_8.CO_2H$. This last named acid is a disagreeably smelling oil, and is converted by the action of bromine and silver oxide into *butyrofuronic acid*, $C_9H_{12}O_5$, a substance readily soluble in water, and reduced by phosphorus and hydriodic acid into *a*-azelaic acid.[2]

*Furfur-butylene*, $C_4H_3O.C_4H_7$, is produced when isobutyric anhydride is heated with furfurol and potassium isobutyrate. It is a colourless oily liquid which boils at 153°, and has a peculiar odour resembling that of the beetle *Carabus sycophanta*.[3] If to its solution in glacial acetic acid a concentrated solution of potassium nitrite be added, the compound $C_8H_{10}O.N_2O_3$ is produced, a substance which crystallizes well, and on reduction in

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* x. 355, 695, 1358.
[2] Baeyer & Tönnies, *Ber. Deutsch. Chem. Ges.* x. 1364; Tönnies, *ib.* xii. 1200.
[3] Baeyer and Tönnies, *ib.* x. 1364.

hydrochloric acid solution yields the hydrochloride of the base $C_8H_{10}O(OH)NH_2$. Hence the addition-product possesses the formula $C_4H_3O.C_4H_7.(NO)(ONO)$.[1]

899 *Constitution of the Furfuryl Compounds.*—These contain the group $C_4H_3O$, which in accordance with Baeyer's suggestion is termed "furfur." Its constitution may be arrived at from the following considerations. Furfurol acts in all its relations in an exactly analogous manner to benzaldehyde, a substance which belongs to the aromatic group, and contains its six atoms of carbon arranged in the form of a ring. It may therefore be assumed that in the furfuryl compounds the four atoms of carbon form a similar closed chain. The simplest member of this group is tetrol, $C_4H_4O$, a substance which is not attacked by the alkali metals, and therefore does not contain hydroxyl. The action of phosphorus pentachloride on pyromucic acid also shows that "furfur" contains neither the hydroxyl group nor the carbonyl group.

The formation of dehydromucic acid from mucic acid may therefore be explained as follows:

$$\begin{matrix} CH(OH)CH(OH)CO_2H \\ | \\ CH(OH)CH(OH)CO_2H \end{matrix} = \begin{matrix} CH.C.CO_2H \\ \| \quad |\!>\!O \\ CH.C.CO_2H \end{matrix} + 3H_2O.$$

By separation of carbon dioxide this then yields pyromucic acid and tetrol:

$$\begin{matrix} CH.CH \\ \| \quad |\!>\!O \\ CH.C.CO_2H. \end{matrix} \qquad \begin{matrix} CH.CH \\ \| \quad |\!>\!O. \\ CH.CH. \end{matrix}$$

Pyromucic acid unites with bromine to form a tetrabromide:

$$\begin{matrix} CHBr.CHBr \\ | \quad \diagdown\!>\!O \\ CHBr.CBr.CO_2H, \end{matrix}$$

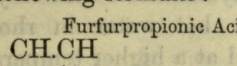
whilst on oxidation it yields fumaric acid:

$$\begin{matrix} CH.CH \\ \| \quad \diagdown\!>\!O \\ CH.C.CO_2H \end{matrix} + 3O = \begin{matrix} CH.CO_2H \\ \| \\ CH.CO_2H \end{matrix} + CO_2.$$

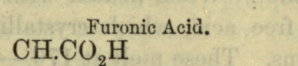
[1] Tönnies, *Ber. Deutsch. Chem. Ges.* xi. 1511.

And the acids produced from furfuryl-acrylic acid will possess the following formulæ:

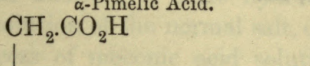
Furfurpropionic Acid.



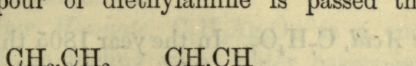
Furonic Acid.



α-Pimelic Acid.

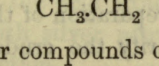


Pyrrol is produced by heating ammonium succinate; and also when the vapour of diethylamine is passed through a red-hot tube:

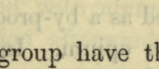


The other compounds of the pyrrol group have the following constitution:

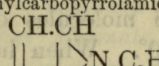
Carbopyrrolamide.



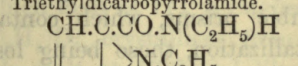
Carbopyrrolic acid.



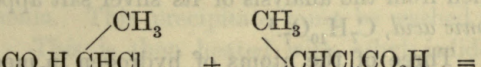
Diethylcarbopyrrolamide.

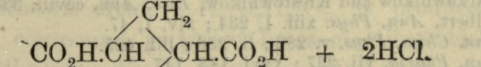


Triethyldicarbopyrrolamide.



900 *Tetrylene-Dicarboxylic Acid*, $C_4H_6(CO_2H)_2$. The ethyl salt of this acid, which is also known as *homoitaconic acid*, is obtained in small quantity, together with that of ethyl-lactic acid and the sodium salts of the two acids, by the action of dry sodium ethylate on the ethyl salt of *a*-chlorpropionic acid. The formation of the acid is explained by the following equation:





The ethyl salt is a pleasantly smelling liquid, which boils at 230°. When heated with strong hydrochloric acid it yields the free acid, which crystallizes from hot water in rhombic prisms. These melt at 170°—171°, and at a higher temperature sublime in fine needles. This acid is isomeric with hydromuconic acid, from which it differs in the fact that it does not unite with hydrogen, bromine, &c.[1]

## MECONIC ACID GROUP.

901 *Meconic Acid*, $C_7H_4O_7$. In the year 1805 this acid was discovered by Sertürner in opium (*Μηκώνιον*),[2] and was afterwards more completely examined by Robiquet,[3] and by Liebig.[4] It is now obtained as a by-product in the preparation of the alkaloids contained in opium. In order to purify the crude acid it is recrystallized from warm dilute hydrochloric acid, in which it is in the cold less soluble than in pure water. The acid is next converted into the ammonium salt, and this is then decomposed by hydrochloric acid.[5]

Meconic acid dissolves in four parts of boiling water, and on cooling the solution it separates out in micaceous scales or small rhombic prisms, which contain three molecules of water of crystallization, these being lost at 100°. When heated more strongly meconic acid loses carbon dioxide, and is converted into comenic acid, $C_6H_4O_5$, and pyromeconic acid, $C_5H_4O_3$. Very minute quantities of ferric chloride impart a deep red colour to solutions of meconic acid and its salts. This colouration is not destroyed on addition of auric chloride, as is the case with the similar colouration produced by thiocyanic acid.

When sodium amalgam is added to a solution of meconic acid, the latter takes up hydrogen, and a non-crystallizable acid is obtained, which from the analysis of its silver salt appears to be *hexhydromeconic acid*, $C_7H_{10}O_7$.[6]

*Meconates.* Three of the atoms of hydrogen in meconic acid are capable of replacement by metals, and Liebig therefore

[1] Markownikow and Krestownikow, *Lieb. Ann.* ccviii. 333.
[2] Gilbert, *Ann. Phys.* xiii. 1, 234; xiv. 1, 47.
[3] *Ann. Chim. Phys.* v. 232; li. 236; liii. 425.
[4] *Ann. Pharm.* vii. 237; xxvi. 113, 147.
[5] Mennel, *Journ. Prakt. Chem.* [2], xxvi. 449.
[6] v. Korff, *Ann. Chem. Pharm.* cxxxviii. 191.

considered it to be a tribasic acid. Later researches have however shown that it contains together with two carboxyl groups, one hydroxyl, the hydrogen of which can be replaced by metals. The basic salts thus produced possess a yellow colour.

*Normal Potassium Meconate*, $C_7H_2K_2O_7$, is readily soluble in hot water, and separates out on cooling in lustrous silky needles or laminæ. On the addition of some hydrochloric acid to the cold concentrated solution of the normal salt, or of caustic potash solution to an excess of meconic acid solution, the acid salt $C_7H_3KO_7$ is obtained in fine needles. If, however, an excess of the caustic potash be employed, then the yellow basic salt, $C_7HK_3O_7$, is thrown down.

*Normal Silver Meconate*, $C_7H_2Ag_2O_7$, is a snow-white precipitate, which on boiling with water passes into the yellow basic salt, $C_7HAg_3O_7$. The latter salt is also formed when a solution of the acid exactly neutralized with ammonia is precipitated with silver nitrate, the solution afterwards exhibiting an acid reaction.

*Normal Ethyl Meconate*, $C_7H_2(C_2H_5)_2O_7$, is obtained by passing a stream of hydrochloric acid gas into a mixture of one part of the anhydrous acid and two parts of absolute alcohol until the acid ethyl meconate which is in the first place precipitated is redissolved. The normal salt crystallizes from hot water in small plates or flattened prisms which melt at 111°·5 (Mennel).

*Acid Ethyl Meconate*, $C_7H_3(C_2H_5)O_7$, crystallizes from hot water in colourless needles which melt at 179°, and, like the foregoing compounds, yields a red colouration with ferric chloride. If silver nitrate be added to its solution, *silver ethyl meconate*, $C_7H_2Ag(C_2H_5)O_7 + H_2O$, is formed, and this crystallizes from hot water in needles.

*Triethyl Meconate*, $C_7H(C_2H_5)_3O_7$, is prepared from the salt $C_7HAg(C_2H_5)_2O_7$, which is obtained as a yellow precipitate by first adding the requisite quantity of silver nitrate to a hot solution of the normal ethyl salt, and then exactly neutralizing with ammonia. This precipitate must be washed and dried in the dark. This is then heated with ethyl iodide, when the triethyl salt is obtained, which crystallizes from dilute alcohol in prisms melting at 61°.

*Ethyl Meconic Acid*, $C_7H_3(C_2H_5)O_7$, is produced when the preceding compound is boiled for some time with water. It forms small prisms, has a strongly acid reaction, and, as is also the case with the triethyl salt, yields no colouration with ferric

chloride. It melts at 200°, giving off carbon dioxide. This acid is metameric with acid ethyl meconate:

Ethyl Meconic Acid. $C_5HO_2\{^{(CO_2H)_2}_{OC_2H_5}$.

Acid Ethyl Meconate. $C_5HO_2\{^{CO_2.C_2H_5}_{CO_2H}$ $^{}_{OH}$.

*Meconamic Acid*, $C_5HO_2\{^{CO.NH_2}_{CO.OH}$ $^{}_{OH}$. The basic ammonium salt of this acid is thrown down as a yellow precipitate when an excess of ammonia is added to a concentrated hot solution of acid ethyl meconate. On decomposition with hydrochloric acid the free acid is produced, and this separates from hot water in warty concretions, which contain one molecule of water of crystallization. It is not decomposed by cold caustic soda solution, but on heating the mixture ammonia is evolved and sodium meconate produced (Mennel).

902 *Comenic Acid*, $C_6H_4O_5$, is formed when meconic acid is heated to 200°—220°, or when it is boiled with strong hydrochloric acid. It dissolves in somewhat above sixteen parts of boiling water, and crystallizes out on cooling in prisms or plates, which are but little soluble in cold water. Ferric chloride imparts a blood-red colour to solutions of the free acid and its salts. Like meconic acid it unites with hydrogen, but the product has not been further examined.

*Comenates.* Comenic acid is a monobasic oxyacid, and like meconic acid forms not only normal but also basic salts, which almost all crystallize easily.

*Ethyl Comenate*, $C_6H_3O_5(C_2H_5)$, is obtained by passing hydrochloric acid gas into absolute alcohol in which comenic acid is suspended. It crystallizes from boiling water in quadratic prisms which melt at 126°·5, but volatilize at a lower temperature than this. Its solution is coloured a deep red by ferric chloride. If a stream of nitrogen trioxide be passed into anhydrous ether containing the free acid in suspension, *ethyl nitrocomenate*, $C_6H_2(NO_2)O_5(C_2H_5)$, is obtained; this forms small yellow needles which melt at 147°, and dissolve readily in hot water. Its solution is coloured red by ferric salts. With various bases it yields yellow salts, which crystallize well.[1]

If ethyl comenate be heated with acetic anhydride to 150°,

[1] Reibstein, *Journ. Prakt. Chem.* [2]. xxiv. 278.

*ethyl acetocomenate*, $C_5H_3(OC_2H_3O)O_2(CO_2.C_2H_5)$, is obtained. This crystallizes in needles which melt at 104°. It yields no colouration with ferric chloride, and is readily split up by water into acetic acid and the ethyl salt.

*Amidocomenic Acid*, $C_5H_2(OH)O_2(NH_2)CO_2H$, is produced by the action of tin and hydrochloric acid on ethyl nitrocomenate It crystallizes from hot water in lustrous needles, which with a little ferric chloride give an indigo-blue colouration, this being changed to red on the addition of more of the reagent. It unites with hydrochloric acid, forming a salt which crystallizes in micaceous scales.

*Comenamide*, $C_5H_2(OH)O_2(CO.NH_2)_2$. The corresponding ammonium compound is produced by the action of ammonia on the ethyl salt, and this on treatment with hydrochloric acid yields the amide, which is purified by recrystallization from boiling water. It forms small white plates and contains one hydrogen atom which may be replaced by metals.

*Comenamic Acid*, $C_6H_5NO_4 + 2H_2O$, is isomeric with comenamide, and is obtained by boiling comenic acid with an excess of ammonia:

$$C_5H_2(OH)O_2(CO_2H) + NH_3 = C_5H_2(OH)O(NH)CO_2H + H_2O.$$

The ammonium salt is of course formed in this reaction, and this is then decomposed by hydrochloric acid. The free acid crystallizes from hot water in colourless lustrous tables, which effloresce on exposure to air, and its solution is coloured purple by ferric chloride. Like comenic acid it forms two series of salts. When heated with zinc dust, *pyridin*, $C_5H_5N$, is formed, a base which it will be more convenient to describe in the sequel.[1]

*Chlorcomenic Acid*, $2C_6H_3ClO_5 + 3H_3O$, is formed by passing chlorine into water containing comenic acid in suspension. It dissolves readily in water, and crystallizes in long four-sided prisms, which lose their water at 100°, and at a higher temperature melt and then blacken and decompose. It yields with ferric chloride the same colouration as that given by comenic acid, and its salts are distinguished from the corresponding comenates by their greater solubility.[2]

*Bromcomenic Acid*, $2C_6H_3BrO_5 + 3H_2O$, is obtained by the

[1] Lieben and Haitinger, *Ber. Deutsch. Chem. Ges.* xvi. 1263. See also Ost, *Journ. Prakt. Chem.* [2]. xxvii. 257.

[2] How, *Edinb. Phil. Trans.* xx. part II. 225.

action of bromine water on comenic acid or meconic acid. It resembles chlorcomenic acid, but is less soluble than the last-named acid.[1]

By the continued action of bromine and water an acid is obtained which has the empirical formula of dibrompyromeconic acid; but it cannot be this, as on heating with water it is easily transformed again into monobrommeconic acid. Mennel assumes that it contains an atom of bromine replacing the hydrogen of the hydroxyl, and terms it therefore *bromoxylbromcomenic acid*, $C_5HBrO_2(OBr)CO_2H$. It dissolves readily in water and alcohol, and crystallizes in fine rhombic tables. Its solution does not yield any immediate colouration with ferric chloride, but on longer standing, or at once on heating, the liquid assumes a red colour, bromcomenic acid being formed.[2]

When the last-named acid is boiled with hydrochloric acid or hydrobromic acid, *oxycomenic acid*, $C_5HO_2(OH)_2CO_2H$, is formed. It crystallizes from water either in long needles which contain three molecules of water, or in short prisms which contain only one molecule of water of crystallization. With ferric chloride it first gives a blue colouration, which changes to red on further addition of the reagent. It is a monobasic acid, but, like meconic acid, it forms three series of salts.[3]

903 *Pyromeconic Acid*, $C_5H_4O_3$, was discovered by Sertürner in 1817, but was for some time considered to be identical with meconic acid, its individuality being first recognized by Robiquet.[4] For its preparation anhydrous meconic acid is heated to 300° or higher, and a current of carbon dioxide is passed through the apparatus in order to bring the pyromeconic acid into the receiver and to prevent the temperature rising to too high a point. The distillate contains some acetic acid, comenic acid,[5] and other products. In order to purify it, the acid is redistilled in small quantities at a time, and is then crystallized from hot water.[6]

Pyromeconic acid crystallizes in large prisms which melt at 117° and dissolve readily both in water and alcohol. They

[1] *Ann. Chem. Pharm.* lxxx. 85; lxxxiii. 356.
[2] *Journ. Prakt. Chem.* [2], xxvi. 466.
[3] Ost, *Ib.* [2], xxiii. 440.
[4] *Ann. Chem. Pharm.* v. 90.
[5] This was at first considered to be paracomenic acid (Stenhouse, *Chem. Soc. Mem.* ii. (1844), 1), but Ost has found that the substance is identical with comenic acid.
[6] Ost, *Journ. Prakt. Chem.* [2], xix. 177.

sublime even at the ordinary temperature, but more readily at 100°, and the liquid boils between 227° and 228°. The aqueous solution, which has only a weak acid reaction, yields with ferric chloride a blood-red colouration.

*Pyromeconates.* Pyromeconic acid does not contain the carboxyl group, but an hydroxyl, the hydrogen of which can be replaced by metals. The compounds so formed unite with a second molecule of pyromeconic acid to form the so-called acid salts. All the pyromeconates are unstable bodies. They darken on exposure to light, and are decomposed when boiled with water. The alkaline salts readily decompose in presence of free alkali, formic acid being produced (Ost).

When pyromeconic acid and acetyl chloride are heated together, *acetopyromeconic acid*, $C_5H_3O_2(OC_2H_3O)$, is produced; it forms colourless prisms, which melt at 91° and dissolve readily in water, but on heating the solution it is easily split up into pyromeconic and acetic acids. The solution does not yield a colouration with ferric chloride.

When hydrochloric acid gas is passed into an ethereal solution of pyromeconic acid, the compound $C_5H_4O_3$,HCl separates out in small needles. Water decomposes this product into its constituents.

If concentrated sulphuric acid be added to an ethereal solution of pyromeconic acid, the following compounds are produced according to the quantity added: viz., either $C_5H_4O_3$,$SO_4H_2$, crystallizing in needles, or $2(C_5H_4O_3)$,$SO_4H_2$, obtained in the form of prisms. Both substances are at once decomposed by water (Ost).

Concentrated nitric acid acts energetically on pyromeconic acid, large quantities of prussic acid and some oxalic acid being formed.[1] Under certain conditions nitromeconic acid, shortly about to be described, is produced.

904 *Brompyromeconic Acid*, $C_5H_3BrO_3$, is formed by the action of bromine water on an aqueous solution of pyromeconic acid, and crystallizes from hot water in short prisms or tables. Its solution yields a deep red colouration with ferric chloride.[2]

*Iodopyromeconic Acid*, $C_5H_3IO_3$. On the addition of chloride of iodine to a solution of pyromeconic acid the iodo-acid separates out in small colourless plates. These are readily soluble in hot water, and their solution acquires a dark-red colour on addition of ferric chloride. By using an excess of

[1] Brown, *Phil. Mag.* [4], viii. 201. [2] Brown, *Chem. Soc. Journ.* vi. 78.

chloride of iodine, Brown obtained a yellow crystalline precipitate which he described as iodomecone, $C_3H_4I_8O_3$, but doubtless this product was simply iodoform :

$$C_5H_4O_3 + 7ICl + 3H_2O = 2CHI_3 + 3CO_2 + HI + 7HCl.$$

*Nitropyromeconic Acid*, $C_5H_3(NO_2)O_3$, is obtained by adding from 2 to 3 parts of pure concentrated nitric acid to a well-cooled solution of 4 parts of pyromeconic acid in 12 parts of glacial acetic acid. At first crystals separate out, which probably consist of meconic nitrate. After a short time, however, a powerful reaction commences, and, on cooling, the nitro-compound separates out in crystals. These are purified by recrystallization from hot absolute alcohol, the solution being quickly cooled, as on long heating, either with alcohol or water, the compound is decomposed. It forms small light yellow prisms, which are but difficultly soluble in cold water. Its solution has a deep yellow colour, and yields a blood-red colouration with ferric chloride. Nitropyromeconic acid is monobasic, forming yellow salts, which explode when heated.

*Amidopyromeconic Acid*, $C_5H_3(NH_2)O_3$. If the nitro-acid just described be treated with tin and dilute hydrochloric acid, and the tin be then precipitated with sulphuretted hydrogen, a solution is obtained of the hydrochloric acid compound of amidomeconic acid, which on evaporation is obtained in large rhombic prisms, having the composition $C_5H_3(NH_2)O_3, HCl + H_2O$. This, when treated with ammonia, yields the amido-acid, which crystallizes from hot water in long needles. Its neutral solution yields, with a little ferric chloride, a beautiful indigo-blue colouration; on further addition of the reagent, the colour becomes green, and then blood-red. The solution reduces silver nitrate with separation of metallic silver.[1]

*Nitrosopyromeconic Acid*, $C_5H_3(NO)O_3$. If absolute ether be saturated with nitrogen trioxide, and the solution then shaken up with a little finely-powdered pyromeconic acid, the liquid, which is at first clear, afterwards deposits an orange-yellow crystalline precipitate of *nitrosodipyromeconic acid*, $C_5H_3(NO)O_3 + C_5H_4O_3$, which, by the further action of nitrogen trioxide, is converted into nitrosopyromeconic acid.

Nitrosodipyromeconic acid is stable only in absence of light, in the presence of which it is decomposed with formation of prussic acid. This last-named acid, together with nitrogen

[1] Ost, *Journ. Prakt. Chem.* [2], xix. 177.

trioxide, carbon dioxide, and other gases, is also formed when the aqueous solution of the nitroso-acid is evaporated, there being produced at the same time smeary decomposition-products, free pyromeconic acid, and a compound of equal molecules of the last-named acid and oxypyromecazonic acid (Ost).

905 *Oxypyromecazonic Acid*, $C_5H_5NO_4$. The double compound just described is obtained in larger quantity when the nitroso-compound is mixed with water to a paste, and sulphur dioxide passed in. It crystallizes in acute monoclinic tables, and is only difficultly soluble in cold water. When boiled with chloroform, pyromeconic acid passes into solution, and the same decomposition takes place when heated alone to 120°.

Oxypyromecazonic acid crystallizes from hot water, either in dazzling white needles which contain one molecule of crystallization water, or in the anhydrous form in short prisms. It occurs less frequently in needles containing two molecules of water of crystallization. Like pyromeconic acid, it forms two series of salts, uniting with acids more easily than the former acid. Ferric chloride imparts to its solution an intense dirty violet colour, and its alkaline solution yields on exposure to the air a fine blue precipitate, which, however, soon becomes discoloured.

*Pyromecazonic Acid*, $C_5H_5NO_3$, is formed in small quantity, together with the amido-acid, in the reduction of the nitro-acid. It is, however, better obtained by the action of hydriodic acid on oxypyromecazonic acid. It crystallizes in fine rhomic tables, and forms a diacetyl compound.

906 *Pyromecazone*, $C_5H_3NO_3$, is produced when concentrated nitric acid is added to pyromecazonic acid suspended in ether, the whole being kept well cooled. The product is insoluble in ether, but dissolves readily in water. The solution stains the skin violet, and has a peculiar smell, somewhat resembling that of iodine. It crystallizes from absolute alcohol, or from spirit, in small needles, containing one molecule of alcohol. Pyromecazone passes readily into pyromecazonic acid by the action of sulphurous acid.

When the last-named acid is treated with nitric acid in the presence of glacial acetic acid, the pyromecazone which is first formed passes into solution on further addition of nitric acid, and after a short time compact yellow prisms of *nitropyromecazone*, $C_5H_2(NO_2)NO_3 + H_2O$, separate out. In aqueous solution this substance decomposes slowly in the cold, and quickly if heated to 30°–40°, carbon dioxide being evolved, and *nitropyromecazonic*

*acid*, $C_5H_4(NO_2)NO_3$, being precipitated. This acid may, however, be obtained in larger quantity and without the evolution of gas by reduction with sulphur dioxide. It is a monobasic acid which crystallizes from solution in a large quantity of water, in golden-yellow tablets. With ferric chloride it yields a blood-red colouration.[1]

907 *Chelidonic Acid*, $C_7H_4O_6$, was discovered by Probst[2] in celandine (*Chelidonium majus*), and more closely examined by Lerch.[3] It is contained in largest quantity at the time of flowering, and occurs partly in the free state and partly as calcium salt, together with malic acid. It is somewhat difficultly soluble in cold, but dissolves readily in hot, water, and on slow evaporation separates out in silky needles containing one and a half molecules of water. On slowly cooling, it is obtained in small interlaced needles which contain one molecule of crystallization water. When exposed to air it slowly becomes anhydrous. On heating to 150° it loses water, and above 220° carbon dioxide is evolved, a new acid being formed which has not been more closely examined.

Chelidonic acid differs from meconic acid by containing one atom less oxygen. Like the last-named acid it forms three series of salts, those containing two equivalents of metal being the most stable.

*Potassium Chelidonate*, $C_7H_2K_2O_6$, crystallizes in small, easily soluble needles. If caustic potash be added to its solution, a yellow crystalline precipitate of the salt $C_7HK_3O_6$ is produced.

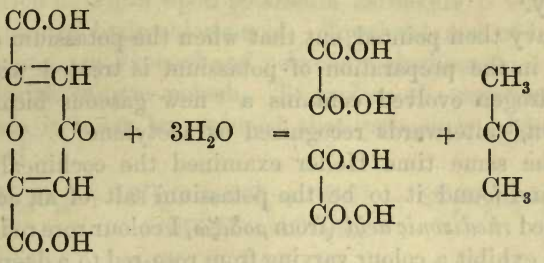
Barium chloride, lead acetate, and silver nitrate yield amorphous yellow precipitates when added to an ammoniacal solution of the acid.

According to Lieben and Haitinger, however, these so-called tribasic salts of chelidonic acid belong to a new acid, produced by taking up the elements of water and containing two hydroxyls besides two carboxyl groups, this, new acid in the free state readily passing into chelidonic acid.

If chelidonic acid be boiled with ammonia, *chelidonamic acid*, $C_7H_7NO_6$, is produced, a body standing in the same relation to chelidonic acid as comenamic acid to comenic acid, and like the first-named, yielding pyridin when heated with zinc dust.[4]

[1] Ost, *Journ. Prakt. Chem.* [2], xxiii. 263.
[2] *Ann. Chem. Pharm.* xxix. 116. [3] *Ib.* lvii. 273.
[4] Lieben and Haitinger, *Ber. Deutsch. Chem. Ges.* xvi. 1259; Lietzenmayer, *Journ. Prakt. Chem.* [2], xxvii. 292.

By boiling with lime, chelidonic acid is completely resolved into acetone and oxalic acid (Lieben and Haitinger), and from this the following constitutional formula for chelidonic acid may be deduced:



As will be further explained under pyridin, the above formula explains in a simple manner the relation between these two bodies.

## Acids derived from Potassium Carboxide.

908 Berzelius and Wöhler were the first to observe that in the preparation of potassium by Brunner's method a grey or black porous mass is formed. Gmelin noticed that this body changes colour on exposure to air, first becoming green and afterwards yellow; and by the addition of a small quantity of water he obtained a yellow solution, whilst a cochineal-red powder remained behind, a substance which had already been noticed by Berzelius and Wöhler. In the solution he ascertained the presence of the potassium salt of a peculiar acid, and, as the acid itself as well as many of its salts exhibited a yellow colour, he gave to it the name of *croconic acid* (from κροκόν, saffron).[1]

This subject was then further investigated by Liebig, who stated that he had already expressed the opinion that carbon monoxide could be regarded as a radical, of which carbonic acid and oxalic acid were oxidation products, whilst phosgene was its chlorine compound. He then continued: "In the pursuit of this idea I have arrived at most remarkable and interesting results, which would seem to prove that these resemblances are not confined to the compounds just described." He found in fact that pure carbon dioxide combines with heated potassium, forming a black mass which is violently decomposed by water,

[1] *Pogg. Ann.* iv. 31.

hydrogen being evolved, together with some hydrocarbon, as the gas burns with a strongly luminous flame. On evaporating the solution he obtained potassium croconate, and potassium oxalate, and at the same time he noticed the formation of the cochineal-red body.[1]

E. Davy then pointed out that when the potassium carboxide formed in the preparation of potassium is treated with water, the hydrogen evolved contains a "new gaseous bicarburet of hydrogen," afterwards recognized as acetylene.[2]

At the same time Heller examined the cochineal-red substance and found it to be the potassium salt of an acid which he termed *rhodizonic acid* (from ροδιζω, I colour rose red), because its salts exhibit a colour varying from rose-red to a deep carmine-red.[3] He also further examined croconic acid, and these two acids were then made the subjects of investigation by several other chemists.

By passing carbon monoxide over warmed potassium, Brodie found that at about 80° arborescent crystalline growths made their appearance on the metal, the whole finally forming a grey crystalline mass. Up to this point the absorption of gas was slow, but after this the action became violent, and the grey mass was transformed, with evolution of heat, but without change of form, into the dark red compound $(COK)_n$, a substance decomposed by water with extreme violence, and often undergoing sudden spontaneous decomposition. As the grey compound formed at first is so easily decomposed, it has not been found possible to obtain it in the pure state; its formula, however, is most probably $(COK_2)_n$.[4]

Lerch, who employed the potassium carboxide obtained in the preparation of potassium, found that this substance is not affected by dry air, but that in moist air it oxidizes, the black mass becoming first grey, then again black, and passing through green and red until finally it becomes yellow. No further change then takes place, and the product yields only croconic and oxalic acids. If, however, the black mass be treated with hydrochloric acid, air being excluded, colourless trihydrocarboxylic acid is produced:

$$C_{10}K_{10}O_{10} + 10HCl = C_{10}H_{10}O_{10} + 10KCl.$$

[1] *Ann. Chem. Pharm.* xi. 182.
[2] *Brit. Assoc. Reports*, 1836, p. 62.
[3] *Journ. Prakt. Chem.* iii. 193.
[4] *Chem. Soc. Journ.* xii. 269.

From this reaction it might be assumed that potassium carboxide is the potassium salt of this acid. But as this acid is tetrabasic, potassium carboxide must contain six potassium atoms combined in a different manner to the rest.[1]

The action of water upon potassium carboxide is very different from that of hydrochloric acid. Equal volumes of hydrogen and acetylene are evolved and potassium rhodizonate is formed together with caustic potash. To explain the reaction which takes place it must be assumed that potassium carbonate is also formed:

$$2C_{10}H_{10}O_{10} + 12H_2O = 3H_2 + 3C_2H_2 + 2C_5H_2K_2O_6 + 8KOH + 4CO_3K_2.$$

909 *Trihydrocarboxylic Acid*, $C_{10}H_{10}O_{10}$, is best obtained by reducing the compound next to be described by means of zinc and sulphuric acid or sulphuretted hydrogen. That it may also be got from freshly obtained potassium carboxide has already been stated. In its preparation air must be excluded. It crystallizes in needles possessing a silky lustre, and dissolves much more readily in water than in alcohol. The solution exhibits an acid reaction. In the moist state or in solution it acquires a red colour by absorption of oxygen, and this is also the case with its salts.

*Dihydrocarboxylic Acid*, $C_{10}H_8O_{10}$, is the first product of oxidation of the preceding compound. For its preparation, potassium carboxide is decomposed in presence of air by means of alcohol containing hydrochloric acid, and the red solution produced is evaporated. It forms either pure black crystals exhibiting a metallic lustre, or thin, transparent yellow trichroic crystals. These do not alter on exposure in the air, provided this be free from ammonia. The acid dissolves readily in hot water, the solution exhibiting a red-violet dichroism. Its salts oxidize readily, forming compounds of the following acid.

*Carboxylic Acid*, $C_{10}H_4O_{10}$, is not known in the free state, as, when its salts are decomposed by acids, it is converted into rhodizonic acid by taking up water:

$$C_{10}H_4O_{10} + 2H_2O = 2C_5H_4O_6.$$

*Potassium Carboxylates.* The normal salt, $C_{10}H_4O_{10}$, is red in colour and is obtained by the oxidation of the black potassium

[1] Lerch, *Wien. Akad. Ber.* xlv. [2], 721; Abstract, *Ann. Chem. Pharm.* cxxiv. 20.

dihydrocarboxylate. The monacid salt, $C_{10}HK_3O_{10}$, forms green crystals, whilst the diacid salt, $C_{10}H_2K_2O_{10}$, is a red powder.

910 *Rhodizonic Acid*, $C_5H_4O_6$, forms hard, colourless crystals containing one molecule of water of crystallization, which they lose at 100°, and then become black. The acid dissolves readily in water and alcohol, and its aqueous solution, on warming, becomes first yellow-coloured and then red. Its salts have been examined by Will.[1]

*Acid Potassium Rhodizonate*, $C_5H_2K_2O_6 + H_2O$, forms a soft, cochineal-red-coloured powder. It is difficultly soluble in cold, but dissolves more readily in hot water. Its neutral solution has a dark reddish-yellow colour, which changes to a pale yellow on addition of an alkali. When heated to between 120° and 150° it loses its water of crystallization.

*Acid Barium Rhodizonate*, $C_5H_2BaO_6 + H_2O$, is obtained as a beautiful red precipitate by adding barium chloride to a solut on of the potassium salt. On drying it forms a dark brown powder, which acquires under the burnisher a cantharidine lustre.

*Silver Rhodizonate*, $C_5HAg_3O_6$, is formed as a dark purple-red precipitate by addition of silver nitrate to a solution of the potassium salt, the latter solution which was at first neutral thus acquiring an acid reaction. Rhodizonic acid is therefore a tribasic acid, exhibiting a close analogy to orthophosphoric acid.

911 *Croconic Acid*, $C_5H_2O_5$. This acid, which has been carefully examined by Will and Lerch, is formed when an alkaline solution of rhodizonic acid is evaporated:

$$C_5H_4O_6 = C_5H_2O_5 + H_2O.$$

At the same time oxalic acid is formed together with a brown smeary mass.

It crystallizes from water or alcohol in pale sulphur-yellow grains or plates, which contain three molecules of water and have a bitter acid taste. Its salts have been examined by Gmelin, Heller, Will, and Lerch.

*Potassium Croconate*, $C_5K_2O_5$, crystallizes from hot water in reddish-yellow needles which contain water. These are but little soluble in cold water, and do not dissolve in alcohol. In taste it resembles saltpetre, and it loses its water of crystallization below 100°, becoming of a light lemon-yellow colour.

[1] *Ann. Chem. Pharm.* cxviii. 187.

The *barium* and *calcium* salts are lemon-yellow precipitates, whilst the *strontium* salt crystallizes in plates which are readily soluble in water and alcohol.

*Copper Croconate*, $C_5CuO_5 + 3H_2O$. This characteristic salt is produced when hot solutions of potassium croconate and copper sulphate are mixed together. On cooling it separates out in small rhombic prisms, the faces of which have a semi-metallic lustre and exhibit a deep blue reflection. By transmitted light it has an orange-brown colour. An admixture of smaller crystals also formed presents the appearance of a dark violet powder. When powdered the salt has a lemon-yellow colour, and according as it is more finely powdered it exhibits to a greater degree its peculiar power of reflecting light.[1]

*Silver Croconate*, $C_5Ag_2O_5$, is an orange-red powder, which when heated decomposes with evolutions of sparks.

*Hydrocroconic Acid*, $C_5H_4O_5$, is produced when croconic acid is heated with hydriodic acid, and if the product be poured into alcoholic potash solution, the potassium salt is precipitated. If this be decomposed with an acid and then treated with alcohol-ether, a yellow solution of hydrocroconic acid is obtained, and on evaporation the acid remains as a yellowish-brown viscid mass, exhibiting a strong acid reaction.

*Potassium Hydrocroconate*, $C_5H_2K_2O_5$, crystallizes from hot water in red needles, the faces of which exhibit a bluish-violet lustre. Its blood-red solution acquires a yellow colour in the air, and this takes place quickly in presence of an alkali, potassium croconate being formed together with a little potassium oxalate.

*Barium Hydrocroconate*, $C_6H_2BaO_5$, is a beautiful peony-red crystalline precipitate, which is insoluble in acetic, but dissolves in hydrochloric acid. If the solution be warmed barium croconate crystallizes out (Lerch).

*Hydrothiocroconic Acid*, $C_5H_4SO_4$, is produced by the action of sulphuretted hydrogen on croconic acid. It forms a reddish-yellow gum-like mass, which dissolves readily in water and has a strongly acid reaction. It is a dibasic acid. The salts of the alkali-metals are readily soluble, and crystallize in garnet-red needles with bluish-green and violet lustre; the other salts form red precipitates. By the action of alkalis these salts are transformed into croconates (Lerch).

*Oxycroconic Acid*, $C_5H_8O_9$, was obtained by Will by the action of chlorine or nitric acid on potassium croconate, and he termed

[1] L. Gmelin, *Ann. Chem. Pharm.* xxxvii. 58.

it *leuconic acid*. It forms a gum-like, readily soluble mass, which when heated to 100° or treated with reducing agents again forms croconic acid. The acid *potassium* salt, $C_5H_7KO_9$, is obtained as a difficultly soluble precipitate by saturating a concentrated solution of the acid with potassium carbonate. The *barium* salt, $(C_5H_5O_9)_2Ba_3$, is a yellowish-white precipitate, whilst the *silver* salt, $C_5H_5Ag_3O_9$, is a light yellow precipitate which when dried at 100° acquires a greenish-yellow colour (Will).

The oxycroconates are easily retransformed into croconates, especially if an alkali be present (Lerch).

Nothing is known as to the constitution of the remarkable compounds which have been described in the four preceding pages.

## TETRINIC ACID GROUP.

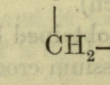
912 The compounds of this group were discovered by E. Demaraçay, who obtained them by the action of bromine on the ethyl salts of methylacetacetic acid and its homologues, and subsequent treatment of the product with alcoholic potash.[1] The acids so obtained exhibit the following remarkable composition:

Tetrinic acid, $(C_4H_4O_2)_3H_2O$.
Pentinic acid, $(C_5H_6O_2)_3H_2O$.
Hexinic acid, $(C_6H_8O_2)_3H_2O$.
Heptinic acid, $(C_7H_{10}O_2)_3H_2O$.

Still more remarkable appears to be the composition of the salts of these acids. Thus tetrinic acid, obtained from ethyl methylacetacetate, yields amongst others the following:

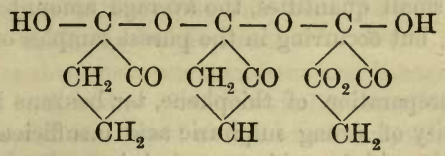
$5(C_4H_4O_2)2(NH_4)_2O$.
$5(C_4H_4O_2)2Ag_2O$.
$5(C_4H_4O_2)2BaO$.
$2(C_4H_4O_2)BaO,H_2O$, &c.

Tetrinic acid would have the following constitution:—



[1] *Ann. Chim. Phys.* [5], xx. 433.

or, including the water which it contains:—



As these acids all crystallize well and are produced by so simple a reaction, the above formulæ do not appear very probable, and consequently the subject has been further investigated by Pawlow[1] and Fittig, and Schultz.[2] These chemists find that tetrinic acid has the constitution $C_5H_6O_3$, being formed from ethyl monobrommethylacetacetate by spontaneous decomposition, slowly in the cold and more quickly on heating, according to the following equation:

$$C_4H_6BrO.CO.OC_2H_5 + H_2O = C_4H_5O.CO.OH + BrH + C_2H_5.OH.$$

It is, like its homologues, a monobasic acid, being most probably *aceto-acrylic acid*, $CH_3.CO.CH = CH.CO_2H$.

From its hot aqueous solution it separates on cooling in feathery crystals, whilst by spontaneous evaporation it is obtained in compact triclinic prisms which melt at 189°. This acid and its homologues give with ferric chloride an intense red-violet colouration.

## THIOPHENE, $C_4H_4S$.

913 Victor Meyer observed[3] that benzene prepared from coal-tar exhibits properties different from those of benzene prepared from benzoic acid,[4] inasmuch as the latter does not yield a blue colouration when treated with isatin and strong sulphuric acid, whilst the former gives, under these conditions, an intense blue colour. He likewise noticed that benzene from tar ceases to give this reaction after it has been well shaken with concentrated sulphuric acid. This singular difference is caused, according to Meyer, by the existence in coal-tar benzene

[1] *Ber. Deutsch. Chem. Ges.* xvi. 1870. [2] *Ib.* xvi. 1939.
[3] Victor Meyer, *Ib.* xv. 2893, xvi. 1465, 1624, 2172, 2968.
[4] Or rather from benzoic acid prepared from the gum, from urine, or from toluol; the acid obtained from benzo-sulphuric acid, on the other hand, gives the reaction in question.

of a sulphur compound, thiophene, $C_4H_4S$, present, however, only in very small quantities, the average amount being about 0·5 per cent., but occurring in the purest samples of commercial benzene.

For the preparation of thiophene, tar benzene is shaken up with a quantity of strong sulphuric acid insufficient to dissolve it entirely; the sulpho-acid converted into the lead-salt, this mixed with sal-ammoniac, and the whole distilled.

The distillate, which consists of a mixture of thiophene and benzene, is subjected to the same treatment, and the oil then obtained dried over calcium chloride and rectified on the water-bath.

Thiophene is also obtained, but in relatively small quantities, when ethylene or acetylene is passed through boiling sulphur. It is a colourless, slightly smelling, powerfully refracting liquid, boiling at 84°, and having a specific gravity of 1·062.

The formation of the characteristic blue colour in contact with isatin and sulphuric acid, with formation of indophenin, is represented by the following equation:

$$C_4H_4S + C_8H_5NO_2 = C_{12}H_7NOS + H_2O.$$

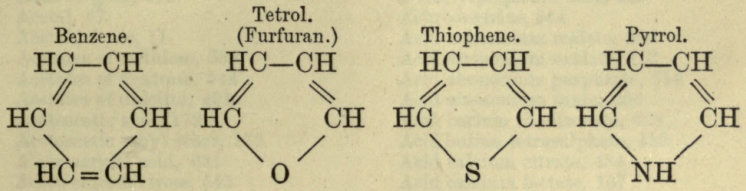
Thiophene gives the same blue reaction with benzoylformic acid, benzil, phenanthrenquinon, and other bodies containing the group CO—CO.

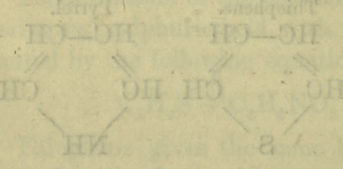
Bromine acts readily on theophene with formation, first of *Monobromthiophene*, $C_4H_3BrS$, and afterwards of *Dibromthiophene*, $C_4H_2Br_2S$, and lastly of *Tetrabromthiophene*, $C_4Br_4S$. The first of these compounds is a colourless oil, boiling at 150°; the second a liquid boiling at 211°, and the third a well-crystallized solid, melting at 112° and boiling at 326°. On treatment with sulphuric acid, thiophene forms a sulpho-acid, $C_4H_3S.SO_3H$, and the potassium salt of this acid yields, on distillation with potassium cyanide, *Thiophenitril*, $C_4H_3S.CN$. This compound closely resembles benzonitril; it boils at the same point, 190°, even possesses the same characteristic smell of bitter almonds, and like this, it can be converted into a corresponding carboxy-acid, $C_4H_3S.CO.OH$. This thiophenic acid melts at 118°, that is 3° below benzoic acid, and boils without decomposition at 258°. In other respects thiophene exhibits close analogy with benzene. Thus it yields condensation products with chloral and methylal, which resemble those of benzene. Indeed, the well known Friedel-Craft's reaction can be obtained with thiophene, so

that by the action of benzoyl chloride and aluminium chlorides a body analogous to benzophenone, viz. *Thienyl-phenyl-ketone*, $C_4H_3S—CO—C_6H_5$, can be prepared.

This close analogy between thiophene and benzene renders it probable that both bodies possess a similar constitution. Thus thiophene may be considered as benzene in which an acetylene-group, CH⎯CH, has been replaced by an atom of sulphur. Its empirical formula, on the other hand, points rather to a relationship with tetrol, $C_4H_4O$, and pyrrol, $C_4H_4.NH$, and although the direct connection between these three bodies has not yet been made out, their analogous behaviour with isatin and sulphuric acid renders such a connection more than probable.

The relations between benzene, thiophene, tetrol, and pyrrol may be exhibited as follows:





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